

PhD Dissertation

Potential-driven generation
of $\text{Ni}(\text{OH})_2$ -type nanoparticles
embedded in non-conductive
poly(Salen) matrices for electrocatalytic
oxidation of ethanol and urea

Monika Mierzejewska





Ph.D. thesis

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for electrocatalytic oxidation of ethanol and urea**

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Metal containing polymers for electrocatalysis and electrochemical sensing (Polimery zawierające jony metali do zastosowań w elektrokatalizie i wykrywaniu elektrochemicznym)



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POLAND

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2. **Monika Mierzejewska (Charązka)**, Kamila Łępicka, Jakub Kalecki, Wojciech Lisowski, and Piyush Sindhu Sharma, 10th International Workshop on Surface Modification for Chemical and Biochemical Sensing (Online), 5 – 9 November 2021, “Nanoparticles Derived from Metal containing Polymers for Ethanol Electrocatalysis”
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(Audience Award for the Best Poster)

List of abbreviations

ACN – acetonitrile
AFC – alcohol fuel cell
CA – chronoamperometry
CE – carbon paste electrode
CP – carbon paper
CPE – carbon paper electrode
CPE' – constant phase element
CV – cyclic voltammetry
DFT – density functional theory
DMA – *N, N*-dimethylacetamide
DMF – *N, N*-dimethylformamide
DMSO – dimethylsulphoxide
ED – electron-donating
EDX – energy dispersive X-ray (spectroscopy)
EFC – ethanol fuel cell
EIS – electrochemical impedance spectroscopy
EOR – ethanol oxidation reaction
EPR – electron paramagnetic resonance
FC – fuel cell
GCE – glassy carbon electrode
HAADF – high-angle annular dark-field
HOMO – highest occupied molecular orbital
HMPT – hexamethylphosphoric triamide
HR – high-resolution
ITO – indium tin oxide
LSV – linear sweep voltammetry
 M^+ Salen – metal Salen complex
ND – not determined
NMP – *N*-methylpyrrolidone
NMR – nuclear magnetic resonance (spectroscopy)
NPs – nanoparticles

OCP – open circuit potential
OER – oxygen evolution reaction
PD – potentiodynamic
PS – potentiostatic
RGO – reduced graphene oxide
SCE – saturated calomel electrode
SEM – Scanning electron microscopy
TEM – Transmission electron microscopy
TMS – tetramethylsilane
UFC – urea fuel cell
UOR – urea oxidation reaction
XPS – X-ray photoelectron spectroscopy

List of symbols

- A – electrode geometric surface area, cm^2
 A' – pre-exponential factor
 A_{CI} – area accessible for counterions
 A_{ECSA} – electroactive surface area
 BE – binding energy, eV
 C – added analyte concentration, mol dm^{-3}
 C_{CP} – capacitance of the carbon paper electrode, F
 C_{dl} – double layer capacitance element, F
 C_{ox} – concentration of the oxidized forms, mol dm^{-3}
 C_{red} – concentration of the reduced forms, mol dm^{-3}
 C_S – specific capacitance, F
 C_0 – concentration in the bulk, mol dm^{-3}
 C^0 – concentration of the electroactive species
 D – diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
 d – doublet
 E – potential, V
 E_0 – potential amplitude, V
 $E^{0'}$ – formal potential, V
 E_{ac} – activation energy, J mol^{-1}
 E_f – final potential, V
 E_i – initial potential, V
 E_k – kinetic energy, J
 ΔE_p – anodic and cathodic peak potential separation
 E_{pa} – peak potential for oxidation, V
 E_{pc} – peak potential for reduction, V
 F – Faraday constant, $96\,500 \text{ C mol}^{-1}$
 f – frequency, Hz
 h – Planck's constant $6.626 \times 10^{-34} \text{ J s}$
 I – current, A
 I_a – anodic current, A
 I_p – peak current, A

I_{pa} – current of the anodic peak, A
 I_{pc} – current of the cathodic peak, A
 I_0 – current amplitude, A
 j – imaginary unit ($j^2 = -1$)
 n – number of exchange electrons in the electrode reaction
 n_0 – number of exchange electrons at the interface of CP electrode | NPs-Ni(OH)₂Salen
 n_u – number of electrons involved in urea electrooxidation
 p – parameter describing the deviation from the ideal behavior of CPE'
 q – charge, C
 q – quartet
 Q_1 – charge of the forward anodic peak, C
 Q_2 – charge of the backward anodic peak, C
 $Q\%$ – *in situ* regeneration ability
 Q_c – cathodic charge, C
 q_c – specific charge, C
 R – gas constant, 8.31 J mol⁻¹ K⁻¹
 R_n – substituent in an organic molecule
 R_{ct} – charge-transfer resistance, Ω
 R_Ω – ohmic resistance, Ω
 s – singlet
 T – temperature, K
 t – time, s
 t – triplet
 ν – scan rate, V s⁻¹
 V – voltage, V
 V_L – volume of electroactive film, m³
 W – spectrometer work function, J
 $Z(\omega)$ – impedance, Ω
 Z_{im} – imaginary part of the impedance, Ω
 Z_{real} – real part of the impedance, Ω

 α – charge-transfer coefficient
 Γ – surface concentration, mol cm⁻²

δ – chemical shift, ppm

ν – electromagnetic field frequency, Hz

φ – phase shift, rad

ω – angular frequency, rad s⁻¹

Abstract (Eng.)

This PhD dissertation presents the fabrication, characterization, and application of Ni(OH)₂-type catalysts embedded in poly(Salen) matrices, named poly[NPs-Ni(OH)₂Salen], for the electrooxidation of small organic molecules such as ethanol and urea. This electrochemical oxidation is of significant importance for energy conversion and wastewater treatment. However, developing efficient catalysts with properly tuned structures that ensure high catalytic activity remains a major challenge. In particular, the fast generation and stability of Ni³⁺OOH-type active sites are crucial for achieving high electrocatalytic performance.

To address this challenge, NiSalen complexes with distinct chemical structures were electrodeposited under potentiostatic and potentiodynamic conditions to prepare poly(NiSalen) precursors with distinct morphologies. Subsequently, poly[NPs-Ni(OH)₂Salen] catalysts were generated *via* a potential-driven transformation of the poly(NiSalen) precursors in alkaline media. The mechanism of this transformation, which had not been previously elucidated, is presented in detail.

Deposition of poly(NiSalen) precursors with various morphologies influenced the arrangement of Ni(OH)₂ NPs embedded in the poly(Salen) matrices. The morphologies of both precursors and the Ni(OH)₂-type catalysts derived from them were imaged using SEM and TEM. These results highlighted interdependencies among the structures of the precursors, the morphologies of the resulting catalysts, and their electrocatalytic performance. Moreover, modifications to the structure of poly(NiSalen) precursors, based on different configurations of methyl substituents at the imine bridge, and the addition of methoxy groups to the aromatic rings, were separately studied to assess their influence on the electrocatalytic activity of the derived catalysts.

However, when urea was electrocatalytically oxidized, additional optimization of the catalyst operating conditions was performed. Taking into account the strong adsorption of the electrooxidation products. The influence of alkaline media concentration on the potential-driven transformation process was investigated by monitoring the *in situ* generation ability of Ni^{3+}OOH -type active centers. The optimal operating conditions of poly[NPs-Ni(OH)₂Salen] catalysts for urea electrooxidation were determined based on comprehensive electrochemical analysis, including multiple scan-rate dependent studies, Tafel slope evaluation, and activation energy determination. At the end, long-term stability tests were conducted in a real system mimicking conditions to confirm the applicability of poly[NPs-Ni(OH)₂Salen] catalysts for the remediation of urea-rich wastewater.

Abstract (Pol.)

Niniejsza rozprawa doktorska przedstawia badania nad wytwarzaniem i charakterystyką katalizatorów na bazie $\text{Ni}(\text{OH})_2$ osadzonych w matrycach poli(Salen), poli[NPs- $\text{Ni}(\text{OH})_2\text{Salen}$], przeznaczonych do elektrochemicznego utleniania małych cząsteczek organicznych, takich jak etanol i mocznik. Reakcje te mają istotne znaczenie dla konwersji energii i oczyszczania ścieków. Jednak opracowanie wydajnych katalizatorów o odpowiednio dostosowanej strukturze, zapewniającej wysoką aktywność elektrokatalityczną, nadal stanowi istotne wyzwanie. Kluczowym czynnikiem warunkującym wysoką efektywność katalizatorów jest szybka generacja i stabilność miejsc aktywnych typu Ni^{3+}OOH .

Aby sprostać temu wyzwaniu, dwa kompleksy Ni-Salenowe o różnej strukturze chemicznej poddano elektropolimeryzacji w warunkach potencjostatycznych i potencjodynamicznych, otrzymując polimery Ni-Salenowe o zróżnicowanej morfologii. Następnie katalizatory poli[NPs- $\text{Ni}(\text{OH})_2\text{Salen}$] wytworzono dzięki elektrochemicznie indukowanej transformacji polimerów Ni-Salenowych przeprowadzonej w środowisku alkalicznym, której mechanizm został szczegółowo wyjaśniony w niniejszej pracy.

Z prekursorów różniących się organizacją przestrzenną warstw polimerowych otrzymano nanocząstki typu $\text{Ni}(\text{OH})_2$ o odmiennej morfologii. Morfologię zarówno prekursorów, jak i otrzymanych katalizatorów zobrazowano z wykorzystaniem mikroskopii SEM i TEM. Uzyskane wyniki wskazały na wzajemne zależności struktury chemicznej i morfologii prekursorów wpływające na aktywność wytworzonych katalizatorów. Ponadto badano wpływ modyfikacji struktury chemicznej prekursorów poli(NiSalenowych), bazując na porównaniu różnych konfiguracji podstawników metylowych przy mostku iminowym, następnie uzupełnionych o dodanie grup metoksyowych do pierścieni aromatycznych, aby ocenić ich wpływ na aktywność elektrokatalityczną finalnie otrzymanych katalizatorów.

W przypadku reakcji elektrochemicznego utleniania mocznika, ze względu na silną adsorpcję produktów reakcji, konieczna była dodatkowa optymalizacja warunków pracy katalizatorów. Monitorowanie zdolności do generowania *in situ* centrów aktywnych typu Ni^{3+}OOH pozwoliło określić wpływ stężenia środowiska alkalicznego na przebieg procesu elektrochemicznie indukowanej transformacji. Optymalne warunki pracy katalizatorów wyznaczono na podstawie kompleksowej analizy elektrochemicznej, obejmującej badania przy zmiennej szybkości przemiatań potencjału, analizę nachylenia Tafela i wyznaczenie energii aktywacji. Na koniec przeprowadzono długoterminowe testy stabilności, aby potwierdzić przydatność katalizatorów poli[NPs-Ni(OH)₂Salen] do oczyszczania ścieków bogatych w mocznik.

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1 Introduction

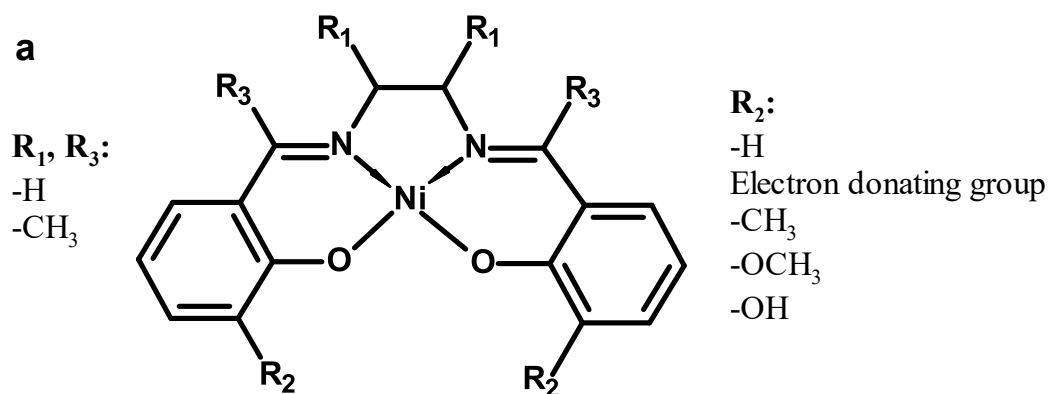
The Salen ligand that coordinates the transition-metal cation is called a metal Salen complex (M^+Salen). These complexes can be utilized in energy conversion as: (i) homogeneous catalysts, (ii) heterogeneous catalysts prepared by immobilizing/depositing those complexes on a support, and converted into catalytically active materials.

M^+Salen complexes electrodeposited as a polymer layer or composite can serve as active materials for electrocatalysis,¹ energy storage,² and conversion.³ Consequently, the growing interest is prompting researchers to design the best chemical structures for Salen metal complexes. Additionally, proper electrodeposition conditions are required to adjust the packing of the polymer's molecular structure.

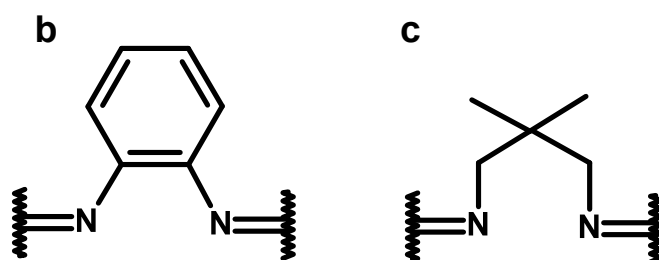
1.1 Nickel-Salen complexes as monomers for Nickel-Salen polymers

Nickel-Salen ($Ni^{2+}Salen$) complexes represent a class of tetradentate [O, N, N, O] symmetrical Schiff bases that coordinate to Ni^{2+} cations. Salen ligands are synthesized through a condensation involving two equivalents of salicylaldehyde or its derivative with one equivalent of ethylenediamine or its derivative.⁴ The tetradentate coordination of the Ni^{2+} occurs through the oxygen and nitrogen atoms in a *cis* configuration. The coordination geometry around the Ni^{2+} is usually square planar.^{5,6} In the unsubstituted $Ni^{2+}Salen$ complex, the interatomic distances of Ni-O and Ni-N are 1.882 Å and 1.889 Å, respectively, indicating that the Ni-N bond is slightly weaker.^{7,8} The structure of the $Ni^{2+}Salen$ -type complex is presented in Scheme 1.1-1a. The condensation of the amine, different from ethylenediamine and its derivatives, with salicylaldehyde or salicylaldehyde derivatives, results in different types of

Ni²⁺Schiff base-based complexes, such as NiSalophen (phenyl ring as an imine bridge) (Scheme 1.1-1b)^{9,10} or NiSalptn (2,2-dimethylpropane as an imine bridge) (Scheme 1.1-1c).^{10,11}



Imine bridges of NiSalophen and NiSalptn complexes



Scheme 1.1-1. (a) Chemical structure of the NiSalen complex, substituted at the imine bridge (R_1), at both 3-positions of the aromatic ring (R_2), and at both α positions of the imine bridge (R_3). Examples of different imine bridges resulting in different NiSchiff base-type complexes (b) NiSalophen-type and (c) NiSalptn-type complexes.

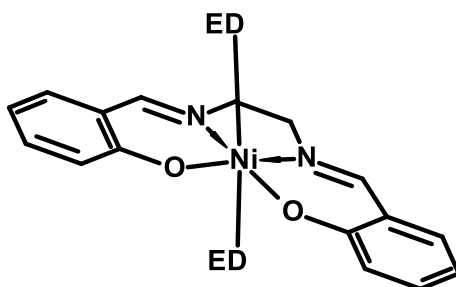
Over three decades ago, the first electrochemically active polymer derived from Ni²⁺Salen complexes was reported.¹² The ‘structurally favored’, i.e., ‘privileged’ NiSalen complexes (Scheme 1.1-1) can be deposited on a conducting surface (working electrode) through oxidative electropolymerization from a solution containing Ni²⁺Salen monomer and organic salt dissolved in a moderately electron-donating (ED) solvent, resulting in the formation of poly(NiSalen)s.^{5,12,13} NiSalen complexes can be electropolymerized under potentiodynamic (PD), potentiostatic (PS), galvanostatic, and pulsed conditions. The electropolymerization and

electrochemical charge transport mechanisms of poly(NiSalen)s were unraveled spectroelectrochemically.¹⁴⁻¹⁶ In the first cycle of PD electropolymerization, when a positive potential is applied, two charge-transfer processes occur. Hence, the process is initiated by the NiSalen monomers oxidation on the conducting working electrode surface to the bisphenolic cation radical (polarons),¹⁴ through the faradaic transfer of one electron,¹⁷ followed by their coupling in the *para* position of aromatic rings¹⁵ (ortho position couplings are also possible for phenyl ring unsubstituted NiSalens).¹⁸ Upon further increase of the applied potential, the bisphenolic cation radicals are oxidized to bisphenolic cations (bipolarons).¹⁵ After changing the polarization direction under PD conditions, two consecutive electroreductions occur: (i) the reduction of bisphenolic cation to bisphenolic cation radicals and (ii) the reduction of bisphenolic cation radicals to the neutral form.¹⁵ After that, from the second cycle, the layer of poly(NiSalen), consisting mainly of oligomers, is formed on the electrode. The consecutive current growth in subsequent cycles evidences the successful deposition of the conducting polymer.¹⁹ During poly(NiSalen) deposition, the resulting positive charge due to the electron withdrawal is compensated by the electrochemical p-type doping, i.e., the ingress of counter-ions from the supporting electrolyte to maintain charge neutrality.²⁰ After the potential sweep, the deposited layer is reduced, and electrochemical dedoping occurs, i.e., counter-ions egress from the polymer.

In PS deposition, a constant potential is applied throughout the process. To achieve successful polymer deposition, the applied potential must exceed the oxidation potential of the monomer to the bisphenolic cation radical. During PS deposition, the polymer layer grows continuously on the electrode surface. The constant formation of radical cations is followed by their coupling to form bisphenolic dications and is accompanied by continuous electrochemical doping to maintain charge neutrality.²¹ The electrodeposition of phenyl ring-substituted poly(NiSalen)s involves the formation of C-C bonds at the *para* positions of the phenyl rings after monomer

oxidation.¹⁸ The formation of poly(NiSalen) cannot occur when the monomer has groups substituted at the *para* or both at the *para* and *ortho* positions of the phenyl ring.¹³ The lack of electropolymerization is also observed when an (ED) compound is present in the solution.

In electrolyte solution prepared in ED solvents, such as *N,N*-dimethylformamide (DMF), dimethylsulphoxide (DMSO), *N*-methylpyrrolidone (NMP), *N,N*-dimethylacetamide (DMA), hexamethylphosphoric triamide (HMPT), and water, the Ni²⁺Salen complex undergoes reversible metal-centered electrooxidation and electroreduction (Ni²⁺ to Ni³⁺).^{6,9,22} During electrooxidation, double axially coordinated ED solvent molecules stabilize the Ni³⁺ valence state.¹³ De Castro and Freire studied the electrochemical behavior of a NiSalophen-type complex in the presence of an ED molecule.⁹ They confirmed the Ni center formal oxidation state of +III with the EPR studies.⁹ Moreover, they proved the axial coordination of two ED molecules to the NiSalophen-type complex.⁹ The general structure of such a complex is presented in Scheme 1.1-2.



Scheme 1.1-2. Axially complexed Ni²⁺Salen with two ED molecules.

The metal center of Salen coordinated Ni²⁺ does not directly participate in the electropolymerization oxidation process in a moderately ED solvent.⁵ However, its presence is essential for depositing the conducting polymer. The Salen ligand (without a metal ion) possesses labile phenol moieties that can repel each other. As a result, the distance required for effective electrooxidation of polymerizing cation radical forms exceeds.¹⁵ The Ni²⁺ center

imposes the square planar geometry of the NiSalen complex, and it does not get involved in the direct oxidation process during electropolymerization.¹⁵

The electrocatalytic behavior of electrodeposited poly(Ni²⁺Salen) can be characterized after transporting the deposited polymer layer to a pure electrolyte solution.^{5,10,14,19} In moderately ED solvents, the conduction path in the poly(NiSalen) is similar to that of polyphenylene, i.e., the Ni center serves as a bridge between the biphenylene moieties.⁵ The poly(NiSalen) layer charge conduction occurs through the Ph-O-Ni²⁺-O-Ph path.^{5,15}

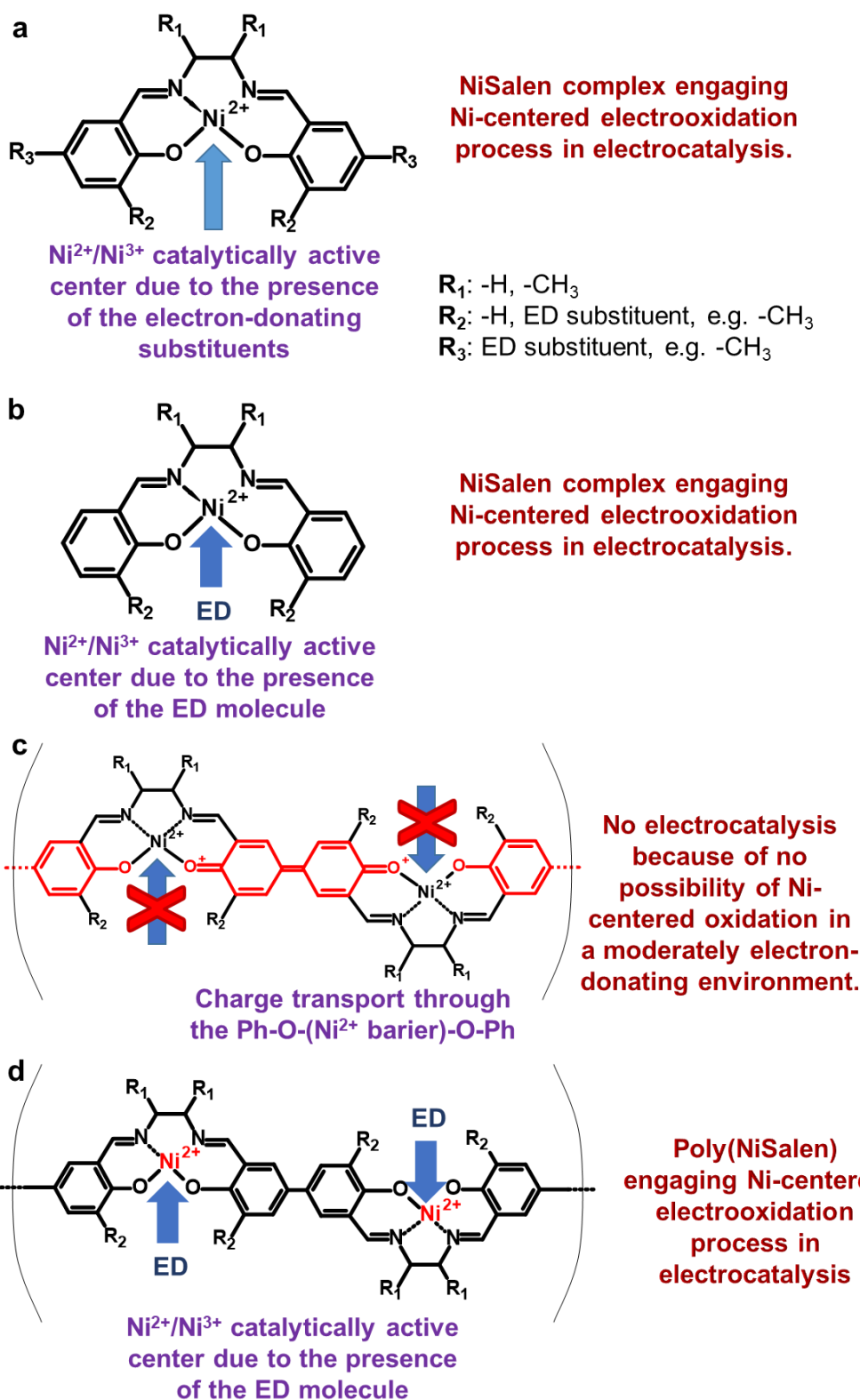
In a moderately ED electrolyte solution, poly(NiSalophen)-based and poly(NiSalptn)-based polymers demonstrate distinct conduction paths from poly(NiSalen)s.¹⁰ This difference is attributed to the differences in substitutions between the imine linkages. The presence of the aromatic rings between those linkages in the NiSalophen polymers forces charge conduction through the -Ph-C=N-aromatic substituent-N=C-Ph- path.^{9,10}

1.1.1 NiSalen complexes in pristine form and immobilized form for catalytic applications

Numerous review articles have highlighted the growing interest in M⁺Salen complexes, particularly NiSalen complexes.^{1,3,23-27} Under certain conditions, the Ni center can be activated. The substitution of ED, bulky substituents like tert-butyl groups at the *ortho* and *para* positions of the phenyl ring shifts the ligand HOMO above the metal's filled d-orbitals, allowing for the removal of an electron from the metal or ligand.²⁸ In other words, the introduction of ED substituents on the Salen ligand can activate the Ni²⁺/Ni³⁺ center, which cannot occur in unsubstituted NiSalen complexes in moderately ED solvents unless an ED molecule, e.g., pyridine,⁹ is present in the system (Scheme 1.1-3 a, b).

NiSalen complexes are widely used to catalyze various reactions, including asymmetric phase transfer alkylations,²⁹ Michael additions,³⁰⁻³² and Mannich-type reactions.³³ Moreover, they are

reported as homogenous electrocatalysts for hydrogen evolution,^{34,35} reduction of alkyl bromides,³⁶ and asymmetric electrochemical carboxylation of acetophenone.³⁷ In the latter example, the effect of *tert*-butyl group substitution in chiral complexes on the enantioselective electrochemical conversion of acetophenone with CO₂ to synthesize chiral 2-hydroxy-2-phenylpropionic acid was investigated.³⁷



Scheme 1.1-3. Structures of NiSalen complexes and poly(NiSalen)s, depending on whether Ni-centered oxidation is involved in the electrocatalytic process (a) Substituted at the phenyl ring, NiSalen complex active in homogeneous electrocatalysis, (b) NiSalen complex unsubstituted at the *para* position, active in homogeneous electrocatalysis, (c) poly(NiSalen)

inactive in electrocatalysis (moderately ED media), (d) a possible way of forcing Ni center oxidation in poly(NiSalen)s.

The active $\text{Ni}^{2+}/\text{Ni}^{3+}$ center is crucial for achieving effective catalysis with Ni^{2+} Salen complexes. The Ni^{2+} Salen complexes, unsubstituted at the *ortho* and *para* positions of the aromatic ring, can be used as catalysts, but first an active $\text{Ni}^{2+}/\text{Ni}^{3+}$ metal site is required. Several reports described the immobilization of NiSalen complexes in different matrices, followed by their transport to the NaOH solution, where the $\text{Ni}^{2+}/\text{Ni}^{3+}$ center is electrocatalytically active (Scheme 1.1-3b).³⁸⁻⁴¹

A few examples described the encapsulation of the NiSalen or NiSalptn complexes into zeolites to prepare heterogeneous electrocatalysts as an alternative to electrodeposited ones (Fig. 1.1-1),^{11,38-40,42} because zeolites have open 3-dimensional frameworks with networks of pores and cavities of molecular dimensions. The preparation of NiSalen-Zeolites electrodes involved mixing complexes with graphite in THF to obtain a suspension. After that, these suspensions were drop-coated on the carbon electrode surface.^{39,40} Few approaches described the preparation of a composite electrode by mixing NiSalen-Zeolites with graphite.^{11,38} The $\text{Ni}^{2+}/\text{Ni}^{3+}$ activity was evident only after cycling working electrode potential, for instance, between 0.1 to 0.8 V vs. SCE.⁴⁰ This multiple potential cycling resulted in the alteration in the active composition of Ni complexes, which was evident by the appearance of anodic and cathodic peaks due to the $[\text{Ni}^{2+}(\text{OH})_2\text{Salen}]\text{Zeolite}/(\text{Ni}^{3+}\text{OOHSalen})\text{Zeolite}$ couple. These electrodes showed interesting catalytic behavior in NaOH_{aq} solution toward the electrooxidation of small molecules. That way, prepared NiSalen complexes encapsulated in zeolites have been used in the electrocatalysis of methanol,^{11,39,40} hydrazine,³⁸ and short-chain aliphatic alcohols.¹¹

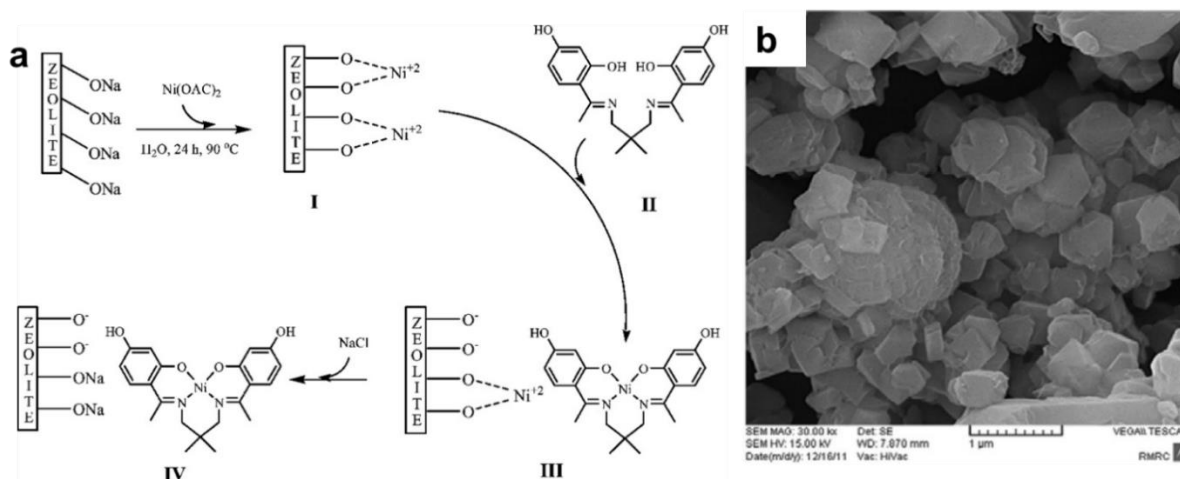
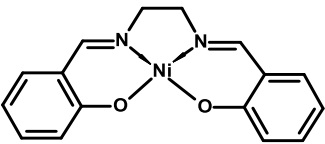
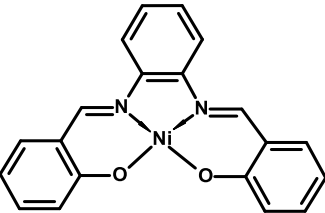
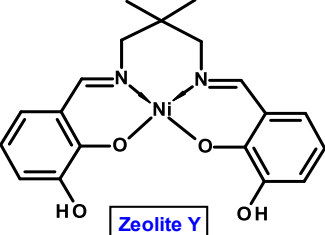
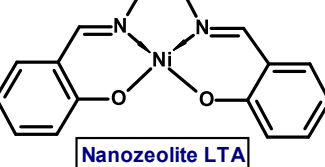
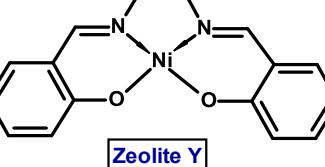


Figure. 1.1-1 (a) Steps of encapsulation of Ni Schiff-base complex in zeolite. (b) SEM image of complex encapsulated in zeolite.¹¹

Another attempt involved drop-coating the NiSalophen complex on the electrode surface, followed by potential cycling in NaOH solution to prepare a catalyst for methanol electrooxidation.⁴³ A different method involved the quaternization of poly(4-vinylpyridine) cross-linked with divinylbenzene by a Ni Schiff-base complex bearing a C–Br function.⁴¹ This synthesized copolymer, covalently grafted with the nickel (II) Schiff base complex, was mixed with a carbon black paste to prepare a catalytically active electrode material. This catalyst was examined for ethanol electrooxidation in NaOH solution. Reports on the use of immobilized and zeolite-encapsulated NiSalen, as well as other Ni Schiff-base composite complexes, are summarized in Table 1.1-1. The electrocatalytic properties of these catalysts were tested in the NaOH solution. In alkaline media, the behavior of these catalysts is analogous to the $\text{Ni(OH)}_2 \rightleftharpoons \text{NiOOH}$ reaction.⁴⁴

Table 1.1-1. Nickel Schiff-base complexes used as precursors for the preparation of catalysts.

Precursor structure	Solution	Immobilization method	Catalyzed molecule	Ref
	0.1 M NaOH	Immobilization by the CV cycling of the complex dissolved in NaOH solution	Methanol, Ethanol, Hydrazine	45
	0.1 M NaOH	Drop coating of the complex on the working electrode	Methanol	43
	1 M NaOH	Encapsulation in Zeolite Y	Methanol, Ethanol, 1-propanol, 2-propanol	11
	0.1 M NaOH	Encapsulation in Nanozeolite LTA	Hydrazine	38
	1.0 M NaOH	Encapsulation in Zeolite Y	Methanol	40

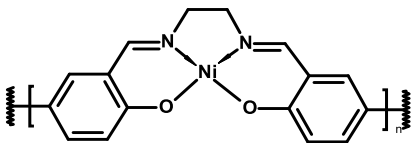
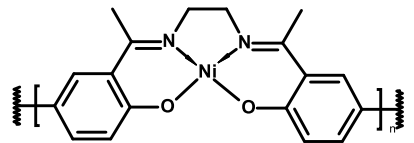
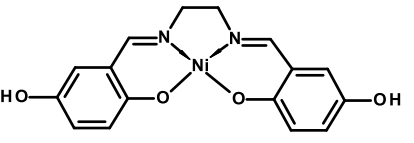
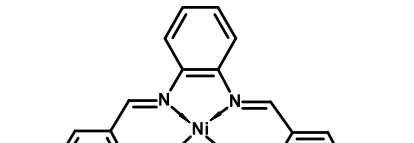
1.1.2 Poly(NiSalen) films for catalysis applications

The NiSalen complexes can be electrodeposited on conducting electrodes to obtain poly(NiSalen) films. In these films, in moderately electron-donor solvents, charge transport

occurs through the Ph-O-Ni²⁺-O-Ph path, with the Ni²⁺ center acting as a bridge between the biphenylene moieties.⁵ This makes poly(NiSalen)s promising materials for energy storage applications,^{10,46-51} especially as active anode materials for supercapacitors.⁵²⁻⁵⁹ However, this conduction path prevents Ni-centered oxidation (Scheme 1.1-3c), limiting their application as catalysts in their pristine form. Therefore, several reports described the fabrication of Ni(OH)₂-based NPs electrocatalysts derived from different poly(NiSalen)s.⁶⁰⁻⁶² By transporting the poly(NiSalen) to alkaline media, it is possible to activate the Ni²⁺/Ni³⁺ center, which is necessary for analyte electrooxidation (Scheme 1.1-3d). However, the mechanism of this potential-driven transformation was not proposed. Derived this way, Ni(OH)₂-based NPs were studied as catalysts for the electrooxidation of small molecules, e.g., methanol, ethanol, and glycerol.⁶⁰ This NPs preparation method is considered advantageous because it is potential-driven and conducted in an aqueous alkaline medium. The poly(NiSalen)s and poly(NiSalophen) utilized up to now for the preparation of Ni(OH)₂-based NPs are listed in Table 1.1-2.

A few reports described complex deposition from aqueous alkaline solution instead of from an organic solvent.^{63,64} Such complexes were substituted with the -OH group at the *para* position (Table 1.1-2). The authors proposed that subsequent polymer layers can be constructed by interconnection *via* Ni-O-Ni linkages.^{63,64} However, previously reported studies showed that the phenolic oxygen is not active in strong ED media,^{9,13} suggesting that this mechanism was misinterpreted. Presumably, complexes substituted with the -OH group at the *para* position polymerize like a phenol.^{65,66} In such cases,^{63,64} during deposition only Ni²⁺/Ni³⁺ center oxidation was seen, and no ligand activity was visible.

Table 1.1-2. Ni Schiff-base polymers used as precursors for the preparation of Ni(OH)₂-based NPs.

Precursor structure	Solution	Catalyzed molecule	Ref
	0.2 M NaOH	Methanol, Ethanol	61
	1.0 M NaOH	Methanol, Ethanol, Glycerol	60
	1.0 M NaOH	Furosemide	67
	0.1 M NaOH	Acetaldehyde	68
	0.1 M NaOH	Ethanol	62
	0.2 M NaOH	Ethanol, Methanol	61
	0.1 M NaOH	Methanol, Ethanol, 2-Methyl-1-propanol	63
	0.1 M NaOH	Methanol, Ethanol, n-butanol, 1-propanol, 2-propanol	64

*Both Schiff-base complexes were deposited from an aqueous solution of 0.1 M NaOH.

1.2 Noble metal-based catalysts

Platinum, palladium, and ruthenium are among the most widely used noble metals in the electrocatalysis of small molecules.^{69,70} Despite their effectiveness, noble-metal-based catalysts suffer from strong adsorption of CO or other electrooxidation intermediates.⁷¹⁻⁷³ As a result, catalyst active sites get blocked, and electrocatalysts exhibit lower electrochemical stability and activity. Moreover, the high price of noble-metal-based catalysts and their limited availability restrict their large-scale application.⁷⁴ This drawback has prompted the search for alternative, more cost-effective materials.⁷⁴ Consequently, there has grown interest in developing catalysts composed of non-noble metals combined with small quantities of noble metals as a cost-effective alternative.⁷⁵⁻⁷⁹ However, this approach still requires the use of low-abundance noble metals.

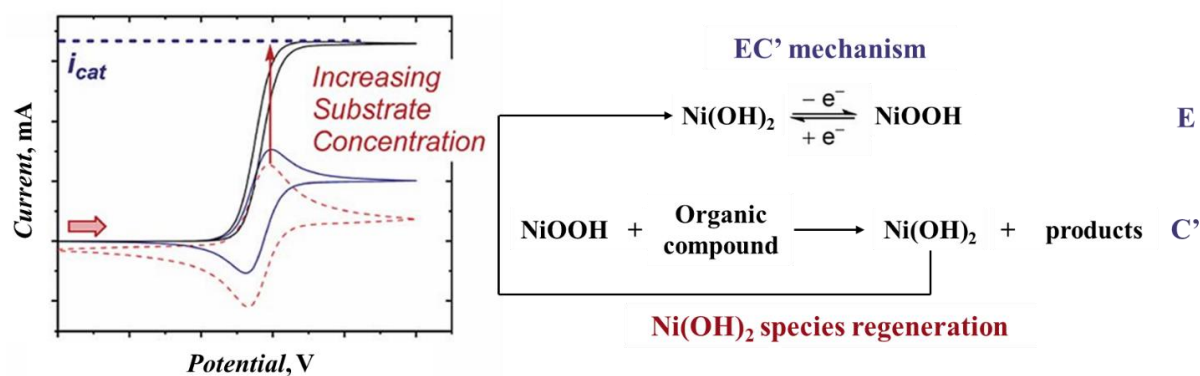
1.3 Catalysts based on nickel hydroxide

A viable alternative to expensive noble-metal-based catalysts is Ni(OH)₂-based catalysts. They are significantly more affordable and exhibit comparatively good catalytic activity toward the electrooxidation of small molecules, similar to those based on noble metals.^{80,81} However, catalysts composed of pure Ni(OH)₂ suffer from too strong adsorption of the electrooxidation intermediates onto the active sites^{61,82-87} and sluggish analyte diffusion due to limited accessibility of the active sites within the catalyst structure.⁸⁸⁻⁹² It was shown that morphology tuning is a successful approach to increasing the number of the catalyst active sites and, as a result, enhancing the catalytic performance.^{93,94}

Ni(OH)₂ catalysts are synthesized using various methods,^{81,95,96} including sonochemistry, sol-gel, and solvothermal methods.⁹⁵ These methods typically result in the deposition of Ni(OH)₂ as a thin film. However, for electrocatalytic applications, decorating the electrode surface with

nanostructured materials is the most accepted approach to creating efficient electrocatalysts.⁹⁷ There are only a few reports in the literature that have demonstrated the direct preparation of isolated Ni(OH)₂ NPs on an electrode surface.⁹⁸

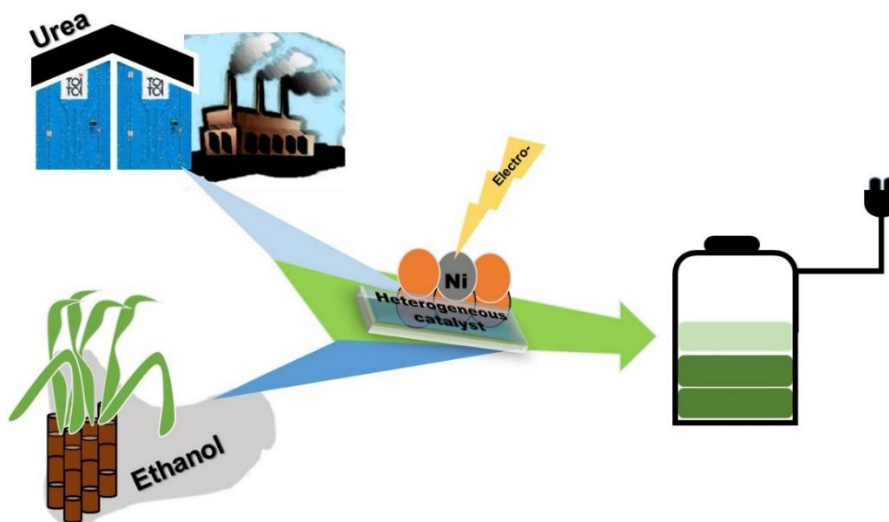
Numerous studies have investigated the mechanism of catalytic electrooxidation of small molecules on Ni(OH)₂-based catalysts.^{99,100} In a catalytic process, a catalyst facilitates the transformation of reactants into products and is subsequently regenerated to its original form. A crucial step in revealing the catalytic mechanism is identifying the catalyst's active sites. The most common mechanism for electrooxidation of small molecules, such as ethanol, on Ni(OH)₂-based catalysts is an EC' mechanism.^{101,102} This mechanism consists of two parts: (i) the electrochemical step (E) – the electrogeneration of NiOOH species, identified as catalyst active sites,^{103,104} and (ii) chemical step (C') – where the chemical oxidation of an organic compound occurs on the NiOOH species, simultaneously with the regeneration of the initial Ni(OH)₂ redox species. In the EC' mechanism, the prime means that the initial catalyst form is regenerated in the chemical step.^{101,102} In this EC' mechanism, the onset potential (the lowest potential at which the catalytic reaction products begin to appear)¹⁰⁵ of the catalytic process is linked to the potential of the Ni(OH)₂/NiOOH oxidation reaction.¹⁰⁶ Scheme 1.3-1 shows a CV response of the Ni(OH)₂ catalyst in the presence and absence of the substrate. In a pure alkaline electrolyte solution, the oxidation and reduction peaks are reversible (Scheme 1.3-1 *red* curve) as only an electrochemical step occurs [Ni(OH)₂ ⇌ NiOOH]. Upon the organic substrate addition, the oxidation peak increases due to the chemical oxidation of the organic compound, whereas the reduction peak decreases (Scheme 1.3-1. *blue* and *black* curves) because NiOOH species are consumed during the compound electrooxidation and are reduced to Ni(OH)₂ in the backward anodic peak.^{107,108}



Scheme 1.3-1. CV responses of a model EC' mechanism of an electrocatalytic oxidation of an organic compound (Substrate). The red curve represents the CV response in the absence of the substrate, and the blue and black curves display responses in the presence of the substrate.¹⁰¹

1.4 Small organic molecules used in catalysis

The earlier section mentioned that different electrocatalysts are fabricated for the electrooxidation of small organic molecules, such as methanol, ethanol, and urea. These electrocatalysts find applications in various areas, including fuel cells (FC), organic synthesis, wastewater treatment, and electrochemical sensing in the medical and environmental fields. Ethanol and urea have emerged as promising clean alternatives to fossil fuels due to their ready availability and safety. This pushes the development of efficient electrocatalysts for the ethanol fuel cell (EFC) and urea fuel cell (UFC), promising technologies for clean energy production (Scheme 1.4-1).^{99,109}



Scheme 1.4-1. Illustration of electrocatalysis of small molecules for energy production.

1.4.1 Ethanol

Ethanol is one of the most promising replacements for gasoline. Accordingly, alcohol fuel cells (AFCs) are among the most promising alternative energy sources. Among the two most popular fuels (ethanol and methanol), ethanol is preferred due to its lower toxicity.^{110,111} Methanol can cause serious health risks like blindness and central nervous system suppression, leading to confusion and drowsiness.¹¹² Moreover, methanol can permeate FC membranes, causing mixed-potential formation at the cathode and reducing the cell's energy yield.¹¹³ Ethanol can be easily obtained through the fermentation process of sugarcane, corn, sugar beet, or other biomass, resulting in bioethanol.¹¹⁴ Furthermore, ethanol possesses a higher energy density compared to methanol.¹¹⁵ Storage and ease of transport make it a more practical fuel than gaseous fuels like hydrogen or natural gas.¹¹⁶ Ethanol's abundant sources, low cost, convenient production, and low operating temperatures further contribute to its suitability.^{111,117}

1.4.2 Urea

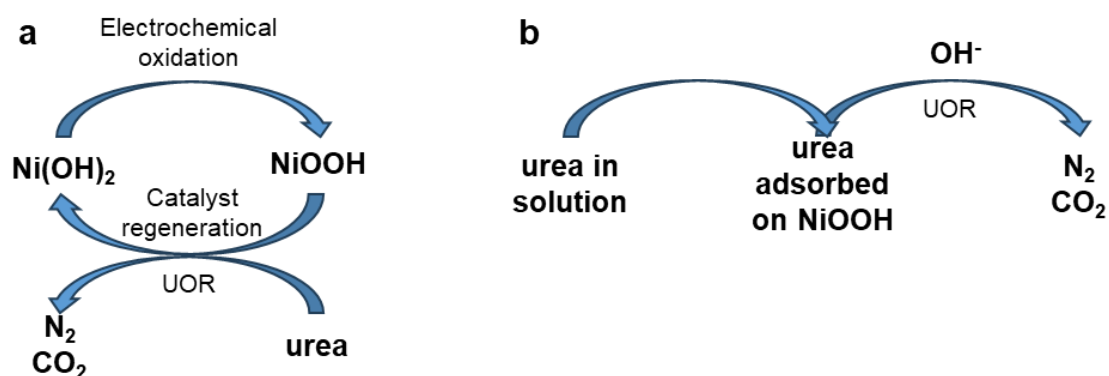
Urea is produced in significant volumes as a byproduct of domestic and industrial waste. The primary sources of urea pollution are fertilizers and human or animal urine, which typically contain 2.0-2.5 wt% urea.¹¹⁸ The average human excretes approximately 11 kg of urea annually.¹¹⁸ The natural decomposition of urea into ammonia and other nitrogen-based pollutants, released into the atmosphere, influences air quality and might cause health risks.^{99,117} This stresses the importance of remediation of such wastewater.

Urea removal can provide opportunities for significant resource recovery, such as nutrients and water. At the same time, it can prevent pollution. Therefore, catalysts capable of simultaneously treating urea-rich wastewater and producing green energy are needed. Urea is considered a good energy source due to its ease of transportation as a solid and its non-flammability.¹⁰⁴ Available methods can remove urea molecules in a single process, such as adsorption, membrane rejection, electrooxidation to CO₂, H₂O, and N₂, or conversion to inorganic ions such as NH₄⁺ or NO₃⁻.¹¹⁹ The operational costs of thermal hydrolysis, wet air oxidation, and membrane separation procedures are high. Electrochemical remediation is an appealing alternative.¹²⁰ However, the electrochemical oxidation process requires a chemically stable catalytic material that does not leach toxic metals and undesirable chemicals through degradation. Moreover, it should be selective, favoring the desired reaction and noncatalytic for undesired reactions. The kinetics of urea oxidation in the absence of a catalyst are slow. Hence, there is a demand for an alternative approach that can utilize urea-rich wastewater to fulfill wastewater treatment needs.

Reports describe two mechanisms of the electrooxidation of urea: (i) an indirect^{82,89,121,122} pathway and (ii) a direct^{107,123,124} pathway. The first, indirect, is also called the regeneration mechanism. According to this mechanism, the oxidation of urea can only occur on the electrogenerated Ni³⁺OOH-based active sites derived from Ni(OH)₂-based forms at

thermodynamically favorable potentials in both forward and backward scans. During the urea electrooxidation, NiOOH active sites are reduced to Ni(OH)₂ (Scheme 1.4-2a). In this mechanism, strong adsorption of OH⁻ and urea electrooxidation products/intermediates occurs at the active sites. As a result, it is crucial to maintain a balance between urea and OH⁻ concentrations. Observing the forward and backward current peak heights allows deducing possible adsorption of reaction products.¹²⁵

The second mechanism, the direct pathway, starts with the simultaneous adsorption of urea and OH⁻ on the catalyst active centers (Ni³⁺OOH-based). Adsorbed urea reacts with OH⁻ species, resulting in the deprotonation of the amine group, and subsequently, the remaining nitrogen is released (Scheme 1.4-2b). Next, adsorbed CO₂ can be oxidized by adsorbed and freely diffusing OH⁻ ions, leading to its release.^{99,107,123}



Scheme 1.4-2. Illustration of two possible mechanisms of urea electrooxidation on Ni(OH)₂ catalyst: (a) indirect, (b) direct pathway.

1.5 Research motivations

As described in earlier sections, the reported catalysts' stability remains unsatisfactory and requires improvement. In electrocatalysis, Ni-based materials have shown promising results; however, substantial improvement is needed to replace noble-metal-based catalysts such

as Pt-, Rh-, and Pd-based catalysts. NiOOH-based NPs are the active species in this catalyst for ethanol and urea electrooxidation. The desired Ni(OH)₂-based catalyst operating in alkaline media needs to provide fast charge-transfer, leading to the electrogeneration of Ni³⁺OOH-based active centers. Hence, the presence and accessibility of these oxidized Ni(OH)₂-based forms, to which the substrate diffuses as quickly as possible, will determine its efficiency.⁸⁹ Therefore, fast electrogeneration of NiOOH-based active centers and their accessibility are necessary to enhance the electrocatalytic activity.

The electrochemical transformation of poly(NiSalen)s in an aqueous alkaline solution is adopted as a new method of preparing Ni(OH)₂-based NPs electrocatalyst.^{60,61} Although this method appears efficient, the reusability of these NPs was limited due to product poisoning.⁶¹ Moreover, in catalysts prepared in this way, NiOOH-based active sites are embedded in a non-conductive matrix, and it is necessary to tune the catalyst morphology to make these active sites accessible.

The effects of the chemical structures of NiSalen complexes on their catalytic activity after NPs generation have not been considered before. NPs' arrangement can be systematically dissected by the proper choice of poly(NiSalen) precursor electrodeposition conditions and by studying changes in their monomer's chemical structure. Challenges involve designing morphologically tuned poly(NiSalen)s and the resulting Ni(OH)₂-type NPs. Tuning electrodeposition conditions by varying the scan rate, number of cycles, and electropolymerization potential range can enable the deposition of poly(NiSalen)s with consistent molecular architecture.¹²⁶ No report described or studied the influence of these parameters during the catalyst precursor preparation step and the resulting electrocatalyst performance.

Furthermore, a proper concentration of alkaline media can drive the binding affinity of substrate oxidation products and increase catalyst durability.^{83,99,107,127,128} However, too high concentration of alkaline media is not preferred from an ecological point of view, and it can

lead to the chemical decomposition of Ni^{3+}OOH -type active centers.^{89,129} Therefore, to achieve the best operation conditions for the structured $\text{Ni}(\text{OH})_2$ -based catalyst, this concentration needs to be optimized. Additionally, the effect of alkaline media concentration during the potential-driven NPs generation step is not studied.^{93,94} The following chapter summarizes the results of those catalysts' structural tuning and operation condition optimizations to fabricate efficient electrocatalysts.

2 Experimental

2.1 Chemicals and materials

- 2,3-dimethyl-2,3-diaminobutane dihydrochloride (98%), $C_6H_{16}N_2 \cdot 2 HCl$ – TCI chemicals
- 2,3-dimethyl-*N, N'*-bis(3-methoxysalicylidene)-2,3-butanediaminonickel, NiSaltMe-3dOMe – synthesis details are provided in Chapter 3.2-1.
- 2,3-dimethyl-*N, N'*-bis(3-methoxysalicylidene)-2,3-diaminobutane, SaltMe-3dOMe – synthesis details are provided in Chapter 3.2-1.
- 2,3-dimethyl-*N, N'*-bis(salicylidene)-2,3-butanediaminonickel, NiSaltMe – synthesized by K. Łępicka.^{15,130}
- 2-hydroxy-3-methoxybenzaldehyde (99%), O-Vanillin, $CH_3OC_6H_3-2-(OH)CHO$ – Sigma Aldrich
- Acetonitrile (anhydrous, 99.8%), ACN, CH_3CN – Sigma Aldrich
- Artificial urine (containing 0.25 M urea) – prepared according to the procedure described by Sarigul et.al.¹³¹
- Carbon paper, CP – FuelCellsETc (College Station, TX)
- Celite® – Sigma Aldrich
- Chloroform (pure p.a., $\geq 98.5\%$), $CHCl_3$ – Chempur
- Chloroform-d (99.8 atom % D, contains 0.03% (v/v) TMS) – Sigma Aldrich
- Dichloromethane (puriss p.a., ACS reagent, 99.9%), CH_2Cl_2 – Sigma Aldrich
- Diethyl ether (anhydrous, $\geq 99\%$), $(C_2H_5)_2O$ – Sigma Aldrich
- Dimethylglyoxime (ACS reagent grade, $\geq 99\%$), $CH_3C(=NOH)C(=NOH)CH_3$ – Sigma Aldrich

- Ethanol (anhydrous), EtOH, CH₃CH₂OH – Sigma Aldrich
- Hexane (anhydrous, ≥ 99%), CH₃(CH₂)₄CH₃ – Sigma Aldrich
- Hydrochloric acid (≥ 33%), HCl – POCH
- Lithium Aluminum hydride (reagent grade, ≥ 97%), LiAlH₄ – Sigma Aldrich
- Magnesium sulfate (anhydrous, pure p.a., 98.5%), MgSO₄ – Chempur
- *meso-N, N'*-bis(3-methoxysalicylidene)-2,3-butanediaminonickel, *meso*-NiSaldMe-3dOMe – synthesis details are provided in Chapter 3.2-1.
- *meso-N, N'*-bis(3-methoxysalicylidene)-2,3-diaminobutane, *meso*-SaldMe-3dOMe – synthesis details are provided in Chapter 3.2-1.
- *meso-N, N'*-bis(salicylidene)-2,3-butanediaminonickel, *meso*-NiSaldMe – synthesized by K. Łępicka.^{15,130}
- Milli Q water (resistance 18.2 MΩ cm)
- Nickel (II) acetate tetrahydrate (reagent grade, 98%), Ni(COOCH₃)₂ × 4 H₂O – Sigma Aldrich
- n-hexane (puriss p.a., ≥ 99%), CH₃(CH₂)₄CH₃ – Sigma Aldrich
- Potassium carbonate (ACS reagent, ≥ 99.0%), K₂CO₃ – Sigma Aldrich
- Reduced Graphene Oxide (RGO) – prepared according to the earlier reported procedure.¹³²
- Sodium hydroxide (pure p.a.-basic, 98.8%) NaOH – POCH
- Tetrahydrofuran (pure p.a., 99.5%), THF, C₄H₈O – Chempur
- Tetra(n-butyl)ammonium hexafluorophosphate (electrochemical grade ≥99%) (TBA)PF₆ – Sigma Aldrich
- Urea (BioReagent ≥ 98%) NH₂CONH₂ – Sigma Aldrich

2.2 Synthesis procedure of 2,3-dimethyl-*N, N'*-bis(3-methoxysalicylidene)-2,3-butanediaminonickel and *meso-N, N'*-bis(3-methoxysalicylidene)-2,3-butanediaminonickel

Already known and widely studied NiSalen complexes, i.e., NiSaltMe^{14,19,133} and *meso*-NiSaldMe,^{15,54,126,130,134} were synthesized by K. Łępicka according to the synthetic methodology developed within her Ph.D.^{130,135} Following the same organic synthesis procedures, 2,3-dimethyl-*N, N'*-bis(3-methoxysalicylidene)-2,3-butanediaminonickel, and *meso-N, N'*-bis(3-methoxysalicylidene)-2,3-butanediaminonickel, abbreviated as NiSaltMe-3dOMe and *meso*-NiSaldMe-3dOMe, were synthesized.

The *meso*-NiSaldMe-3dOMe constituted the new analog of earlier synthesized and studied *meso*-NiSaldMe-3dMe^{18,134} in which the methyl (-CH₃) substituents placed in both 3-positions of *meso*-NiSaldMe phenyl rings were replaced with slightly more ED methoxy substituents (-OCH₃). Moreover, the analog of this new complex, i.e., NiSalen-3dOMe⁶¹ without methyl substituents in the *meso* configuration on the imine bridge, was one of the first to be converted into Ni(OH)₂ NPs catalysts. The NiSaltMe-3dOMe was synthesized to maintain a constant experimental conceptualization order based on comparison of Ni(OH)₂-type NPs catalyst precursors derived from the *meso*-NiSaldMe and NiSaltMe complexes with different configurations of methyl substituents on the imine bridge.

The *meso*-NiSaldMe-3dOMe synthesis involved three steps, and the NiSaltMe-3dOMe synthesis was a two-step procedure. It is because crucial *meso*-diaminobutane dihydrochloride,¹³⁰ necessary for the synthesis of all *meso*-NiSaldMe derivatives, is not a commercial compound. According to that, in the first step of *meso*-NiSaldMe-3dOMe, the *meso*-diaminobutane dihydrochloride was synthesized by the reduction of dimethylglyoxime

with lithium aluminum hydride. Resulting racemic products: D, L-diaminobutane dihydrochloride and *meso*-diaminobutane dihydrochloride were separated by fractional crystallization with methanol. Condensation of 2 equivalents of respective derivatives of salicylaldehyde with 1 equivalent of 2,3-dimethyl-2,3-diaminobutane, or *meso*-diaminobutane, was performed in the second step. Finally, in the third step, the Ni complex with the ligand was prepared. A detailed description of the synthesis is provided in Chapter 3.2-1.

The yields of synthesized products are summarized in Table 3.2-1. The structures of all synthesized compounds were confirmed by nuclear magnetic resonance (NMR) spectroscopy (all NMR spectra are provided in the Appendix). The ^1H and ^{13}C NMR spectra were recorded with the Agilent (400 MHz). Acquired chemical shifts (δ) were registered in ppm with respect to the tetramethylsilane (TMS) signal, corresponding to $\delta = 0.00$ ppm. To denote signal multiplicity, the following symbols were used: s – singlet, d – doublet, t – triplet, and q – quartet.

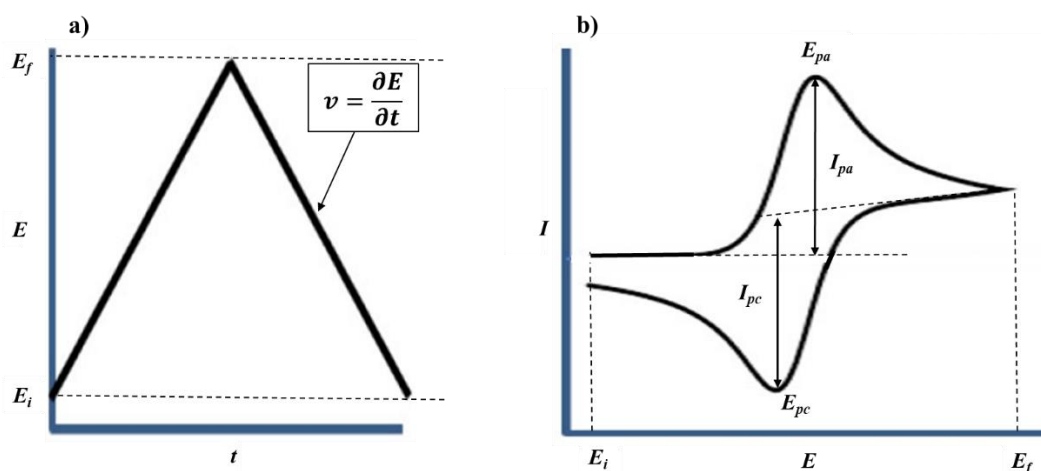
2.3 Experimental techniques and instrumentals

2.3.1 Cyclic voltammetry

Cyclic voltammetry (CV) is the most widely used technique for investigating the oxidation and reduction processes of molecular species. CV provides information on redox processes and heterogeneous electron-transfer reactions. This technique is also very useful for studying electron-transfer-initiated reactions, e.g., catalysis. Moreover, it can be involved in the electrodeposition of polymer, e.g., electropolymerization under PD conditions.

2.3.1.1 The basics

During a CV measurement, the applied potential (E) is linearly changed over time (t) from the initial potential (E_i) to the final potential (E_f) (Scheme 2.3-1a) at a certain scan rate (v). During CV, the current (I) is measured as a function of the applied potential at the working electrode against the reference electrode. This allows investigation of the electrochemical behavior of the studied material in forward and backward scans, providing information on the redox processes occurring during the scanning.¹³⁶ The result of such measurement is presented as a cyclic voltammogram (Scheme 2.3-1b). The appearance of peaks in a voltammogram indicates occurrences of faradaic processes, i.e., oxidation and reduction reactions.¹³⁷



Scheme 2.3-1. a) Wave form showing the time-dependent applied potentials during a CV experiment. b) The current as a function of applied potential in a CV for a reversible process.¹³⁸

2.3.1.2 Electrodeposition of polymer precursors

One method for depositing conducting polymers is the electropolymerization under PD conditions. Polymers can be deposited with different morphologies by varying the number of potential cycles or the scan rate during the electrodeposition.¹³⁹ As a result, deposited polymers have different electrochemical properties and stability. Polymers deposited at higher scan rates during CV showed a rather smooth surface, whereas those deposited at lower scan rates

produced a rougher structure with larger features. By varying the number of cycles, it is possible to obtain polymers indicating different amounts of charge loading.

The amount of charge/charge loading (q) of the deposited polymer can be easily calculated by the integration of the anodic part of the $I(t)$ curve according to Equation 2.3-1:

$$q = \sum_n \int_{t_{1,n}}^{t_{2,n}} I_a(t) dt \quad (2.3-1)$$

Herein, to determine the amount of charge of the deposited poly(NiSalen), only the anodic part was integrated because NiSalen monomers polymerize through anodic polymerization (Figure 2.3-1).

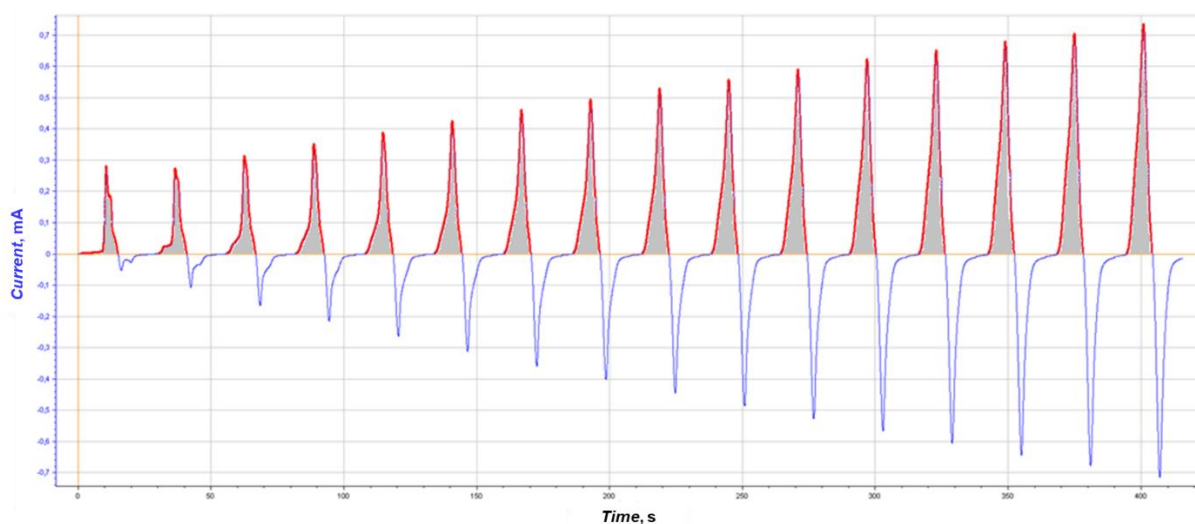


Figure 2.3-1. Current change measured with respect to time during electrodeposition of the poly(NiSalen)-type precursor. The integrated area, marked gray, was considered in the charge calculation.

2.3.1.3 Electrochemical characterization of redox active species at the electrode surface

One of the most useful tools for characterizing redox-active species is a multiple-scan rate experiment. By varying the scan rate and observing resulting current-potential responses, it is

possible to determine whether the electrode process is under diffusion or kinetic control. For an ideally reversible redox process involving electrode-surface-confined species, the oxidation (E_{pa}) and reduction (E_{pc}) peak potentials are equal.¹⁴⁰ However, when the surface-confined species are embedded in a non-conducting matrix, a slight peak separation is expected. The oxidation and reduction processes occurring on the electrode surface require charge neutralization by the counterions freely diffusing in the solution. Hence, resulting in a slight peak potential separation (ΔE_p). At higher scan rates, the counterions diffusion becomes slower and cannot maintain the charge-transfer rate, leading to further increases in ΔE_p . However, the electrode process remains Nernstian in this case.^{140,141}

As an example, if we consider the presence of Ni(OH)₂-based NPs redox active species on the electrode, two main processes can be considered:

- 1) Electrochemical oxidation of the Ni²⁺ to the Ni³⁺, occurring at the first interface of working electrode | Ni(OH)₂-type NPs.
- 2) Chemical oxidation of the analyte, occurring at the second interface of Ni(OH)₂-type NPs | solution.

At the first interface, electrode | Ni(OH)₂-type NPs oxidation of Ni²⁺ to the Ni³⁺ occurs. When this diffusion-controlled electrooxidation/electroreduction process is fast and reversible,^{82,88,89} the potential can be expressed by the Nernst equation (Equation 2.3-2):¹³⁷

$$E = E^{0'} + \frac{RT}{nF} \ln\left(\frac{C_{ox}}{C_{red}}\right) \quad (2.3-2)$$

Where $E^{0'}$ is a formal potential, R is a gas constant, T is a temperature, n is the number of exchange electrons in the electrode process, F is a Faraday constant, and C_{ox} and C_{red} are concentrations of the oxidized and reduced forms.

For a diffusion-controlled redox process, the peak current is linearly increasing with v or $v^{1/2}$, whether the diffusion limitation arises from a finite or a semi-infinite regime.^{142,143} The peak current occurs at $E = E^0$, and for a finite diffusion regime, I_p is given by Equation 2.3-3:

$$I_p = \frac{n^2 F^2}{4RT} v V_L C^0 \quad (2.3-3)$$

Where v is a scan rate, V_L is the volume of the electroactive film, and $C^0 = C_{ox} + C_{red}$ is the concentration of the electroactive species in the film.

For a semi-infinite diffusion regime, I_p is given by the Randles-Ševčík equation (Equation 2.3-4):¹³⁶

$$I_p = 0.446 n F A C^0 \left(\frac{n F v D}{RT} \right)^{1/2} \quad (2.3-4)$$

Where A is the electrode area, and D is the diffusion coefficient.

For an electrode-adsorbed species, the current response is described with Equation 2.3-5¹⁴⁰:

$$I_p = \frac{n^2 F^2}{4RT} v A \Gamma \quad (2.3-5)$$

Where Γ is the surface concentration of the adsorbed species.

The electrochemical process can be controlled by the kinetic or diffusion. The charge-transfer is the controlling step in a process under kinetic control. For the electrochemical oxidation of the Ni^{2+} to Ni^{3+} occurring at the electrode | $\text{Ni}(\text{OH})_2$ -type NPs interface, the diffusion of the counterions is the slowest step, and therefore, the process is under diffusion control.^{82,88,89} In this thesis, emphasis was placed on observing whether the current originating from the $\text{Ni}^{2+}/\text{Ni}^{3+}$ oxidation process depends linearly on v or $v^{1/2}$, i.e., whether the diffusion limitation arises from a finite (suggesting a surface process)¹⁴⁴ or a semi-infinite (suggesting a bulk process) regime. In the finite-diffusion regime, the thickness of the electroactive layer is less than or equal to the diffusion layer. In contrast, for the semi-infinite diffusion regime, the thickness of the diffusion

layer is lower than the electroactive layer. These two regimes of diffusion control can be determined by plotting the logarithm of the current against the logarithm of the scan rate. The slope determined from this dependence, 0.5, indicates that the process is under semi-infinite diffusion control, whereas a slope of 1.0 indicates finite diffusion control.^{142,143}

In the presence of the substrate/analyte (e.g., ethanol or urea), it is necessary to consider the process occurring on the second interface of Ni(OH)₂-type NPs | solution. At this interface, the chemical step occurs – oxidation of the substrate/analyte on the electrogenerated Ni³⁺OOH-type centers *via* the EC' mechanism.^{101,107} In this case, the chemical step is irreversible, and the I_p is given by Equation 2.3-6:¹⁴⁵

$$I_p = 2.99 \cdot 10^5 n[(1 - \alpha)n_0]^{1/2} ACD^{1/2}v^{1/2} \quad (2.3-6)$$

Where n is the number of electrons involved in the reaction on the Ni(OH)₂-type NPs | solution interface, n_0 is the number of electrons involved in the reaction on the electrode | Ni(OH)₂-type NPs interface, α is a charge-transfer coefficient, and C is the added analyte concentration.

When a catalytic process is under charge-transfer control, the slope of $\log(I)$ vs. $\log(v)$ will be close to 0.

CV is also employed to study different parameters describing electrocatalyst performance, such as peak current, regeneration ability, and the onset potential, defined as the lowest potential at which the reaction products start to appear.^{105,146} The good electrocatalyst should simultaneously indicate the highest catalytic current and the lowest onset potential.⁹⁹

The temperature dependence of electrochemical reaction rates can be described with the CV measurements carried out at various temperatures using the Arrhenius equation (Equation 2.3-7):¹⁴⁰

$$k = A' \exp\left(\frac{-E_{ac}}{RT}\right) \quad (2.3-7)$$

Where k is the reaction rate constant, A' is the pre-exponential factor, E_{ac} is the activation energy, and T is the temperature. In the electrochemical measurements, the current (I) is proportional to the reaction rate. Therefore, it can be used as a kinetic parameter for Arrhenius analysis. By taking the decimal logarithm, the equation can be rearranged into a linear form (Equation 2.3-8):

$$\log(I) = \log(A') - \frac{E_{ac}}{2.3R} \cdot \frac{1}{T} \quad (2.3-8)$$

Thus, plotting $\log(I)$ vs. $1/T$ gives a straight line, the slope corresponds to $-E_{ac}/2.3R$ (Equation 2.3-9), enabling the determination of the activation energy.

$$\frac{\partial \log(I)}{\partial \frac{1}{T}} = \frac{-E_{ac}}{2.3R} \quad (2.3-9)$$

In order to calculate E_{ac} values, the CV responses were recorded at a scan rate of 50 mV s⁻¹ over the potential range of 0.0-1.0 V vs. Ag/AgCl (3 M KCl), with measurements carried out separately at each temperature. Temperature was controlled using two thermocouples, one inside and one outside the electrochemical cell. The E_{ac} values were determined at 0.45 and 0.50 V (potentials corresponding to the urea electrooxidation).

2.3.2 Linear sweep voltammetry

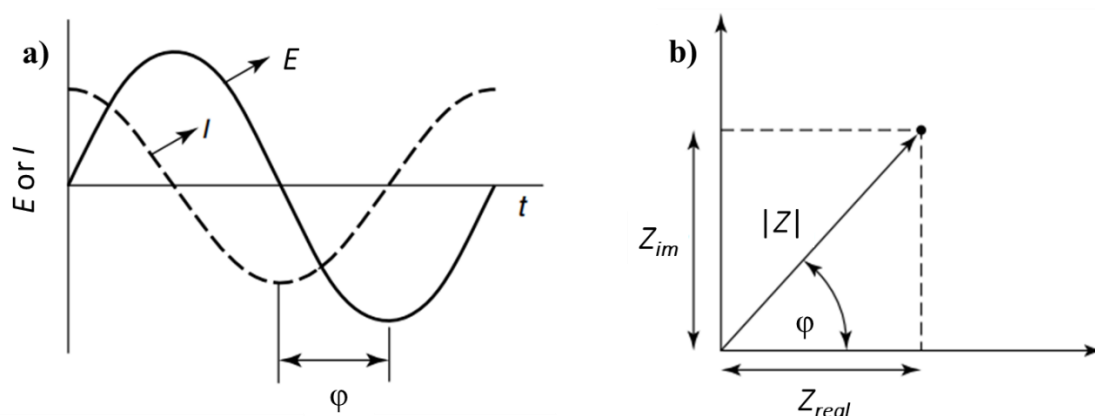
Linear sweep voltammetry (LSV) is a technique used to construct the Tafel plots. In LSV, unlike in the CV, only a forward scan is recorded, without a backward scan. In this technique, the working electrode potential is scanned linearly from the initial to the final value, and current is recorded as a function of potential.

From the LSV data, a Tafel plot [E vs. $\log(I)$ dependence] can be constructed. In addition to the thermodynamic overpotential, the reaction kinetics can be estimated from the Tafel slope. By plotting the overpotential as a function of the logarithm of the current density, the Tafel slope

is estimated. This plot is commonly employed for comparative analysis of electrocatalysts, assessing their efficiency in producing current in response to changes in the applied potential. The smaller the Tafel slope, the more efficiently the current is produced in response to the change in applied potential.¹⁴⁰

2.3.3 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) has many applications in physical electrochemistry, FC development, sensors, corrosion, and batteries. It provides information on reaction parameters, mass transport, coating, and interfacial capacitance measurements. EIS in a three-electrode setup can be utilized to study the electrical behavior of systems at the interfaces of electrode | electroactive species and electroactive species | solution.



Scheme 2.3-2. (a) Changes in the current response as a consequence of the applied sinusoidal potential. (b) Vector projection of the impedance in the complex plane.¹⁴⁷

EIS involves applying a small amplitude alternating potential over a range of frequencies to the working electrode. Applied sinusoidal potential can be described by Equation 2.3-10.

$$E(t) = E_0 \sin(\omega t) \quad (2.3-10)$$

Where E_0 is a potential amplitude, ω is an angular frequency which is 2π times the normal frequency (f), and t is the time.

As a result of the applied sinusoidal potential, the current is generated. This current has the same frequency but is shifted in phase (φ) (Scheme 2.3-2a) and given by Equation 2.3-11:

$$I(t) = I_0 \sin(\omega t) \quad (2.3-11)$$

Where I_0 is the current amplitude.

The impedance [$Z(\omega)$] can be presented on the complex plane (Scheme 2.3-2b) and is defined analogically to Ohm's law applied to direct current measurements, as the ratio of potential and current according to Equation 2.3-12:

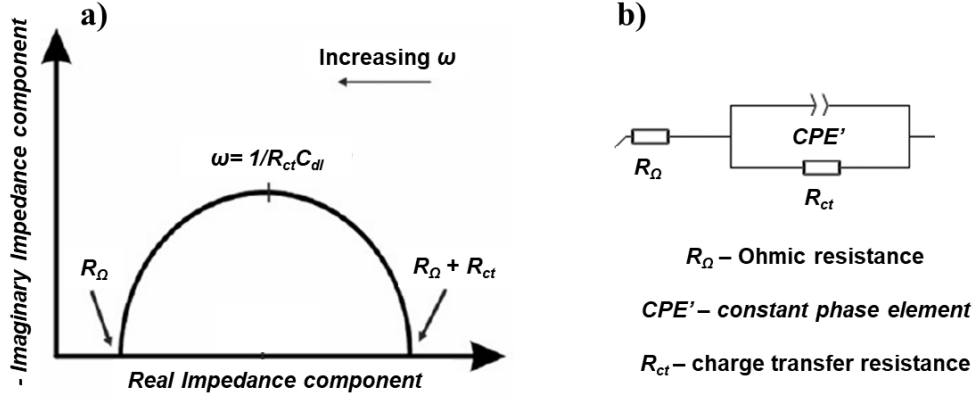
$$Z(\omega) = \frac{E(t)}{I(t)} \quad (2.3-12)$$

And the impedance can be presented as a complex function:

$$Z(\omega) = |Z|(\cos\varphi + j\sin\varphi) = Z_{real} + jZ_{im} = |Z|e^{j\varphi} \quad (2.3-13)$$

Where Z_{real} is the real and Z_{im} is the imaginary part of the impedance, j is an imaginary unit $j = \sqrt{-1}$.

Impedance data are commonly presented in a Nyquist plot, representing the impedance at various frequencies. This plot represents the Z_{real} and $-Z_{im}$ on the vertical and horizontal axes, respectively, in point format. The resulting impedance data can then be fitted to an equivalent electric circuit. This involves adapting the equivalent circuit parameters to experimental data and extracting quantitative information.¹⁴⁸ An example of the Nyquist plot with the theoretically fitted equivalent electric circuit is shown in Scheme 2.3-3.



Scheme 2.3-3. (a) Nyquist plot showing EIS data, and (b) Modified Randles-Ershler equivalent electric circuit composed of electrical elements used for theoretical fitting of the individual electrical circuit element values to the experimental data.¹⁴⁸

The modified Randles-Ershler equivalent electrical circuit shown in Scheme 2.3-3b is composed of the following electrical elements: R_Ω (ohmic resistance), CPE' (constant phase element), and R_{ct} (charge-transfer resistance). The R_Ω element in the circuit describes the combined resistance of the solution, the electrical connection, and the electroactive material.¹⁴⁹ It is usually displayed as a point shifted to more positive directions on the real impedance axis, opposite to the appearance of the point at coordinates 0.0 for $R_\Omega = 0$. Next, the appearance of the semi-circle implied the use of the R_{ct} and CPE' element in parallel because the semi-circle is typical for the charge-transfer process.¹⁴⁸ The high porosity of the studied materials leads to a deviation from an ideal capacitor, implicating the use of the CPE' element instead of the C_{dl} (double layer capacitance) element.¹⁵⁰ Parameter p describes this deviation from the ideal behavior. Its value varies from 0 to 1, where for $p = 1$, the material behaves like an ideal capacitor, and C_{dl} is equal to CPE' .¹⁵⁰ The C_{dl} values can be calculated from the CPE' according to Equation 2.3-14:

$$C_{dl} = CPE' \cdot (\omega'')^{p-1} \quad (2.3-14)$$

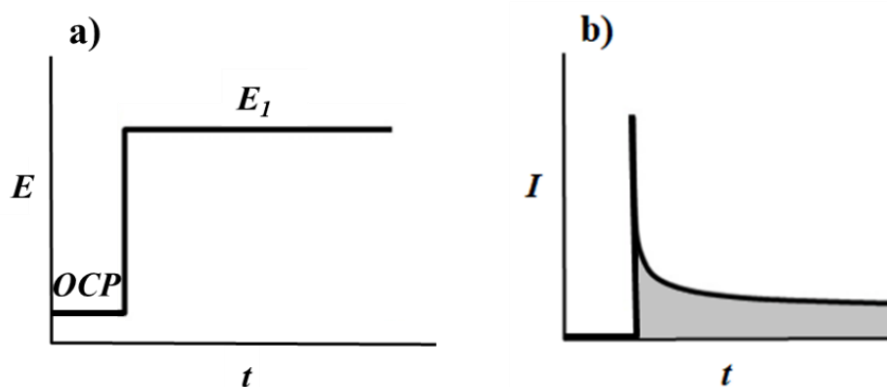
Where ω'' is the maximum frequency of the imaginary part of the impedance.

In this work, EIS measurements were recorded at potentials corresponding to selected states of electroactivity of Ni(OH)₂-type NPs catalysts, in the presence and absence of the analyte, in a suitable electrolyte solution. Before each measurement, the electrode was equilibrated by applying the selected potential for a suitable time, needed to reach current equilibrium. The EIS measurements were carried out in the frequency range from 10 kHz to 10 mHz at a voltage amplitude of 10 mV. EIS data were fitted using the Z_{Fit} function from the EC-lab software with the Randomize + Simplex method. The criterion of the fitting was the smallest value of the χ^2 .

2.3.4 Chronoamperometry

Chronoamperometry (CA) is a technique used to study electrode process mechanisms, measure diffusion coefficients, and electrodeposition of polymers at constant potential under PS conditions, and provide quantitative information about redox processes or insights into mass transport processes.

In this technique, a constant potential is applied to the working electrode, and the resulting current is recorded as a function of time. Scheme 2.3-4a presents the change from the open circuit potential (OCP), where no faradaic processes occur, to the potential E_1 , at which electrochemical processes happen. Scheme 2.3-4b shows the dependence of the current on time after applying a constant potential, E_1 . The integration area required to determine the amount of deposited polymer charge is marked in gray.



Scheme 2.3-4. a) Applied potential as a function of time during CA measurement. b) The resulting current – time response.

In chronoamperometric measurements, the concentration of electrochemically active species near the electrode surface decays with distance, and the arrival of redox-active species to the electrode is diffusion-limited. Because of mass-transport limitations, the faradaic current decays over time. This current is described by the Cottrell equation (Equation 2.3-15):¹⁰²

$$I = \frac{nFAC_0D^{1/2}}{\pi^{1/2}t^{1/2}} \quad (2.3-15)$$

Where C_0 is a bulk concentration of the analyte, and D is the diffusion coefficient. Using the non-modified Cottrell equation is limited to planar electrodes.

2.3.4.1 Electrodeposition of polymer precursors

CA can be used for the electrodeposition of a polymer precursor. Conducting polymers can be deposited by applying a constant potential that exceeds the monomer oxidation potential. By adjusting the electrodeposition time, electroactive films with different charges can be deposited. The charge of the deposited potentiostatically polymer can be calculated by Equation 2.3-16:

$$q = \int_{t_1}^{t_2} I(t)dt \quad (2.3-16)$$

2.3.4.2 Durability test of electrocatalyst in a real system mimicking conditions

The CA is typically used to assess the electrocatalyst's stability. CA has been engaged to mimic the actual operating conditions of a FC by applying a constant potential corresponding to the analyte electrooxidation. This experiment aims to evaluate the long-term performance and durability of the catalyst under conditions similar to those in real system use. Steadiness in measured current density suggests high catalyst stability. However, the durability test can be performed by multiple CV experiments. No decrease in CV peak currents in such an experiment indicates higher stability of electrocatalysts.

2.3.5 Electrochemical setup and general procedures

All electrochemical measurements, i.e., CV, LSV, EIS, and CA, were performed on a BioLogic SP300 potentiostat, controlled by EC-Lab software. For that, a three-electrode setup was used with a V-shape, glass, electrochemical cell. A laminated CP electrode (5 mm diameter) or an RGO-coated CP electrode was used as the working electrode. The RGO was prepared by chemical reduction of graphene oxide with lithium aluminum hydride.¹³² Subsequently, RGO dispersed in DMF was drop-coated onto the CP electrode surface. The RGO-coated CP electrodes were dried under reduced pressure, rinsed with acetonitrile, and stored in a dry environment.⁵⁴ The Pt coil served as the counter electrode. The Ag wire and Ag/AgCl (3 M KCl) electrode, purchased from Metrohm, were used as the reference electrode for the measurements in organic and aqueous solvents, respectively. The deposition conditions for individual poly(NiSalen) precursors are provided in the respective chapters in which they are discussed.

The electrochemically active surface area (A_{ECSA}) of $\text{Ni}(\text{OH})_2$ catalyst can be estimated using the oxalate method proposed by Hall et al.¹⁵¹ This method involves recording a CV in 0.1 M NaOH_{aq} and 0.08 M $\text{C}_2\text{O}_4^{2-}$ at a relatively high scan rate of 150 mV s^{-1} . Such a high scan rate ensures stabilization of the NPs' surface and limits oxalate growth to a monolayer. During the CV, oxalate adsorbs on the $\text{Ni}(\text{OH})_2$ surface by substituting surface hydroxide groups, forming five-membered rings. Taking into account the unit cell parameters (the $\text{Ni}(\text{OH})_2$ forms a hexagonal structure with the Ni-Ni spacing for a $\beta\text{-Ni}(\text{OH})_2$ equal to 3.13 Å),¹⁵¹ and the working electrode geometrical area (0.196 cm^2), the theoretical value of a specific charge (q_c) can be calculated as 38.8 $\mu\text{C cm}^{-2}$. The A_{ECSA} can be determined according to Equation 2.3-17.

$$A_{\text{ECSA}}[\text{cm}^2] = \frac{q [\text{mC}]}{q_c [\frac{\text{mC}}{\text{cm}^2}]} \quad (2.3-17)$$

The q was estimated from the discharging part of a CV curve within a potential window of 0.25-0.58 V, according to Equation 2.3-16.

2.3.6 Scanning electron microscopy

Scanning electron microscopy (SEM) is a technique primarily used to obtain high-resolution images of the surface morphology of polymers and nanomaterials. During SEM imaging, a small area of the sample surface is scanned by a focused electron beam, typically with an energy of 1-50 keV.¹⁵² The electrons interact with the atoms within the sample, thereby producing various signals that can be used to obtain information about the surface's topography and composition. At the same time, images are processed using dedicated software that correlates the beam's position with the intensity of electrons acquired by the detectors and shown on a monitor. In SEM, two types of detectors, the secondary electron detector and the back-scattered electron detector, are used for high-resolution imaging. Secondary electrons are emitted from a near-surface region as a result of inelastic interactions between the sample and the primary

electron beam. The energy of these electrons is usually in the range of 0 – 200 eV.¹⁵² Back-scattered electrons originated from the interactions between the beam and the volume of the sample. These electrons are emitted due to elastic collisions between electrons and atoms, which alter their trajectories. The energy of back-scattered electrons is much higher than that of secondary electrons. The SEM's unique configuration determines its resolution and available imaging modes.

SEM imaging of polymer precursors and Ni(OH)₂-type NPs catalysts was performed using an FEI Nova NanoSEM 450 microscope directly on the CP electrode surface.

2.3.7 Transmission electron microscopy

Transmission electron microscopy (TEM) is used to image the structures of thin samples, typically of 50-100 nm thickness.¹⁵² During TEM imaging, electrons emitted by the source are accelerated in a gun by a high-voltage generator. The usual accelerating voltage used in the TEM is in the range of 100-300 kV. Although measurements are also possible at even higher voltages, such as 1 MV or above.¹⁵² The primary focus of TEM is to capture electrons transmitted through the sample. TEM imaging provides structural information down to the atomic scale. Because TEM detects electrons transmitted through the sample, it is possible to obtain insights into its inner structure, such as its crystal structure and lattice repeat distance,¹⁵³ rather than only surface morphology imaging as in SEM.

The TEM imaging was performed using a Talos F200X microscope equipped with a Super X, energy-dispersive X-ray (EDX) detector. For TEM image recording, Ni(OH)₂-type NPs catalysts were scratched from the CP electrode and deposited on a copper grid.

2.3.8 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a technique used for qualitative and quantitative surface elemental analysis of studied materials (<10 nm). In this technique, x-rays (energies below ~6 keV) are bombarded on the material surface, and the kinetic energy of the emitted electrons is measured.¹⁵⁴ A typical XPS spectrum is called a ‘survey’, where the intensity (counts per second) of the electrons is plotted as a function of their binding energies (eV). This survey spectrum helps in identifying elements on a material surface.

The XPS allows the differentiation of the chemical state of different elements. The parameter that identifies an electron is the binding energy (BE) and can be calculated according to Equation 2.3-18:¹⁵⁴

$$BE = h\nu - E_k - W \quad (2.3-18)$$

Where $h\nu$ is the photon energy, E_k is the kinetic energy of the electron, and W is the spectrometer work function.

XPS spectra were recorded using monochromatic Al K α ($h\nu = 1486.4$ eV) radiation using the PHI 5000 VersaProbe Scanning ESCA Microprobe. The XPS measurements were performed with a 100 μm -diameter X-ray beam, capturing data from an irradiated area of 500 $\times$ 500 μm . High-resolution (HR) XPS spectra were collected using a hemispherical analyzer, employing a pass energy of 23.5 eV, with an energy step of 0.1 eV, and a photoelectron take-off angle of 45° relative to the surface plane. XPS data were analyzed using CasaXPS (v. 2.3.19) software. Peak fitting involved employing a Shirley background and Gaussian/Lorentzian peak shape profiles. To establish a consistent BE scale for all detected spectra, the BE of the C 1s peak was set to 284.8 eV.

2.4 Quantum chemical calculations

Quantum chemical calculations based on density functional theory (DFT) are widely used to investigate the electronic structure of atoms and molecules. Using DFT, bond lengths, angles, and vibrational frequencies can be calculated. By providing insights into electron density distribution, oxidation states, and reaction energetics, DFT enables a deeper understanding of the mechanisms governing catalytic activity.

Single catalytic center of NP-Ni(OH)₂SaltMe and NP-*meso*-Ni(OH)₂SaldMe structure geometry was optimized using semiempirical PM6-D3 (PM6 Hamiltonian),¹⁵⁵ incorporating Grimme empirical dispersion D3¹⁵⁶ method implemented in the MOPAC2016¹⁵⁷ software package. Obtained from semiempirical output geometries were used as an input for DFT calculations.

The DFT calculations were carried out using the Tao-Perdew-Staroverov-Scuseria functional.¹⁵⁸ Consistent with the semiempirical stage, Grimme D3¹⁵⁶ dispersion correction was also applied. The 6-31⁺⁺G(d,p) basis set (Gaussian double-zeta valence basis set with dispersion and diffuse functions) was used.

3 Results and discussion

Results presented in this chapter aim to establish the relationship between the chemical structure of poly(NiSalen) precursors, the conditions of their potential-driven transformation, and the resulting catalytic performance of poly[NPs-Ni(OH)₂Salen] catalysts for the electrooxidation of ethanol and urea. Particular attention was devoted to revealing the mechanism of the potential-driven transformation of poly(NiSalen) precursors into poly[NPs-Ni(OH)₂Salen] catalysts. The influence of the catalyst morphology and the spatial arrangement of Ni(OH)₂ NPs within the poly(Salen) matrices was deeply investigated in relation to catalytic activity.

3.1 Catalytic properties of Ni(OH)₂-type NPs derived from structurally tuned poly(NiSaltMe) and poly(*meso*-NiSaldMe) precursors toward ethanol electrooxidation

This chapter discusses the research work published in *ACS Appl. Mater. Interfaces* 2022, 14, 29, 33768–33786.

Herein, the transformation of poly(NiSaltMe) and poly(*meso*-NiSaldMe) precursors into poly[NPs-Ni(OH)₂Salen] catalysts in alkaline media is described. These poly(NiSalen)s were electrodeposited on laminated CP electrodes⁵⁴ under distinct electrochemical conditions to prepare precursors with different morphologies. Extensive characterization of the poly(NiSalen) precursors and poly[NPs-Ni(OH)₂Salen] catalysts using XPS, SEM, and TEM techniques is described. The suitability of the generated poly[NPs-Ni(OH)₂Salen] catalysts toward ethanol electrooxidation was studied. The chemical structure and precursor morphology were found to influence the structure and electrocatalytic efficiency of the fabricated catalysts. Furthermore, the electrochemical stability of poly(NiSalen) precursors in moderately ED

media¹³⁴ was found to directly affect the ease of their potential-driven transformation into poly[NPs-Ni(OH)₂Salen] catalysts in alkaline media. Moreover, the impact of additional RGO⁵⁴ reinforcement on poly(NiSalen) precursors was investigated.

3.1.1 Poly(NiSalen) precursors electrodeposition

It was found that the tuning of the electropolymerization conditions can affect the morphology of the deposited conducting polymer layers.¹³⁹ Herein, electrodepositions were carried out under different conditions to prepare poly(NiSaltMe) and poly(*meso*-NiSaldMe) with distinct morphologies. Respective poly(NiSalen)s were deposited under multi-scan PD and PS conditions. During the PD deposition, the potential window was 0.0 to 1.3 V vs. Ag/Ag⁺. Table 3.1-1 summarizes details of all the precursor polymers.

Table 3.1-1. Poly(NiSalen)s electrodeposited under different conditions to achieve different morphologies

Polymer deposition condition *	Poly(NiSaltMe)	Poly(<i>meso</i> -NiSaldMe)
Precursor deposited with 29 cycles at a scan rate of 100 mV s ⁻¹	poly(NiSaltMe)-PD _{high}	poly(<i>meso</i> -NiSaldMe)-PD _{high}
Precursor deposited with 16 cycles at a scan rate of 100 mV s ⁻¹	poly(NiSaltMe)-PD _{high} '	poly(<i>meso</i> -NiSaldMe)-PD _{high} '
Precursor deposited with 3 cycles at a scan rate of 2 mV s ⁻¹	poly(NiSaltMe)-PD _{low}	poly(<i>meso</i> -NiSaldMe)-PD _{low}
Precursor deposited with 2 cycles at a scan rate of 2 mV s ⁻¹	poly(NiSaltMe)-PD _{low} '	poly(<i>meso</i> -NiSaldMe)-PD _{low} '
Precursor deposited under PS conditions with high charge	poly(NiSaltMe)-PS _{high} Charge similar to that passed during poly(NiSaltMe)-PD _{high} electropolymerization	poly(<i>meso</i> -NiSaldMe)-PS _{high} Charge similar to that passed during poly(<i>meso</i> -NiSaldMe)-PD _{high} electropolymerization
Precursor deposited under PS conditions with low charge	poly(NiSaltMe)-PS _{low}	poly(<i>meso</i> -NiSaldMe)-PS _{low}

Charge similar to that passed during
poly(NiSaltMe)-PD_{low}
electropolymerization

Charge similar to that passed during
poly(*meso*-NiSaldMe)-
PD_{low} electropolymerization

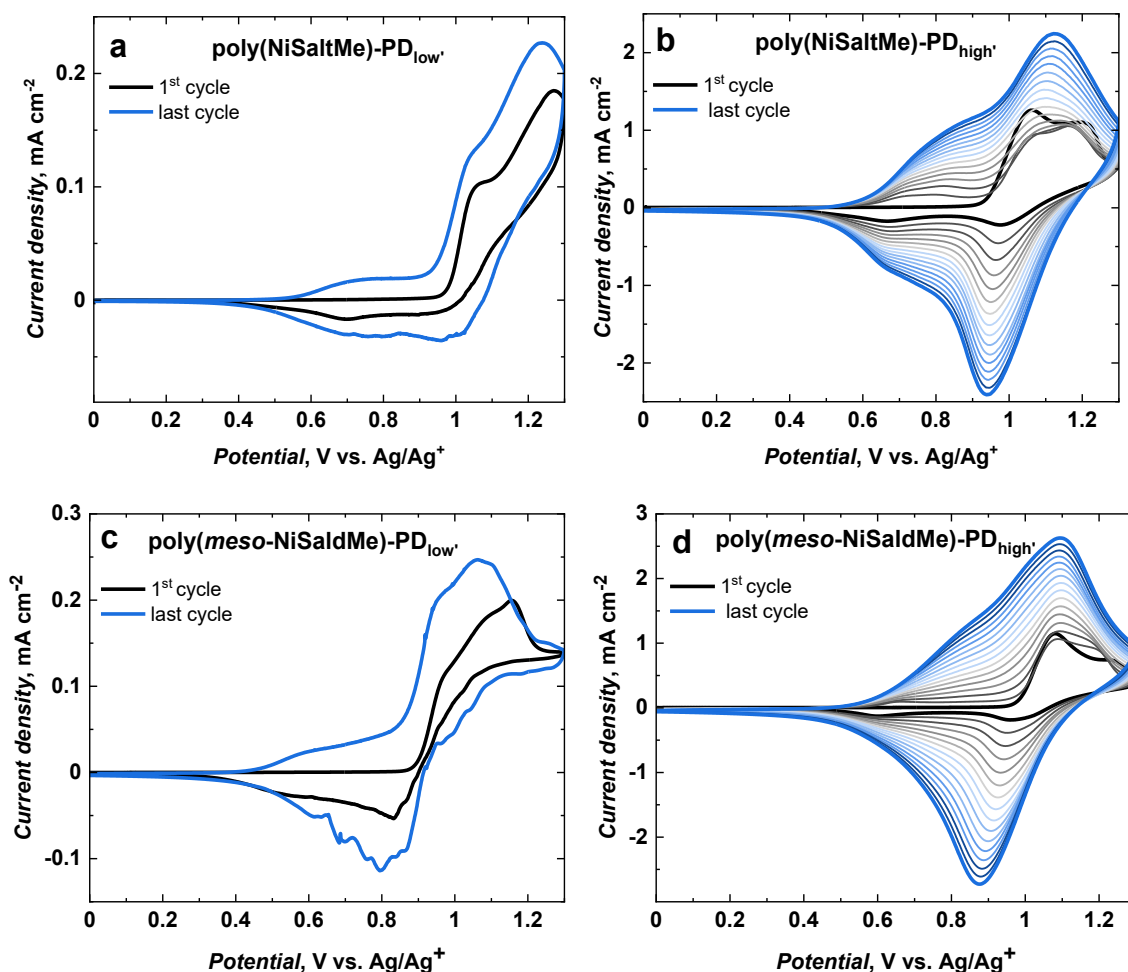


Figure 3.1-1. CV curves showing the oxidative electropolymerization conducted under PD conditions in the potential range of 0.0-1.3 V, at 2 mVs⁻¹ (a, c) low and 100 mVs⁻¹ (b, d) high scan rates. During deposition, the solution contained 1 mM of (a, b) NiSaltMe and (c, d) *meso*-NiSaldMe in 0.1 M TBAPF₆ in ACN.

Figure 3.1-1 presents the oxidative electropolymerization curves of poly(NiSaltMe)-PD_{low}' (Fig. 3.1-1a), poly(NiSaltMe)-PD_{high}' (Fig. 3.1-1b), poly(*meso*-NiSaldMe)-PD_{low}' (Fig. 3.1-1c), and poly(*meso*-NiSaldMe)-PD_{high}' (Fig. 3.1-1d). The current increase in the following polymerization cycles confirmed the successive deposition of conducting polymers. Two anodic and two cathodic peaks were visible in all CV curves in the first cycle. The first anodic

peak, centered at ~ 1.00 V (Fig. 3.1-1a), ~ 1.05 V (Fig. 3.1-1b), ~ 0.97 V (Fig. 3.1-1c), ~ 1.09 V (Fig. 3.1-1d), corresponded to the initial electrooxidation of NiSalen monomers on the CP electrode surface to form bisphenolic cation radicals. The second anodic peak, centered at ~ 1.25 V (Fig. 3.1-1a), ~ 1.15 V (Fig. 3.1-1b), ~ 1.15 V (Fig. 3.1-1c), ~ 1.20 V (Fig. 3.1-1d), was characteristic of the oxidation of bisphenolic cation radicals to bisphenolic cations. The first cathodic peak, centered at ~ 1.00 V (Fig. 3.1-1a), ~ 0.95 V (Fig. 3.1-1b), ~ 1.00 V (Fig. 3.1-1c), ~ 1.19 V (Fig. 3.1-1d) corresponded to the reduction of bisphenolic cations to bisphenolic cation radicals, while the second peak, centered at ~ 0.70 V (Fig. 3.1-1a), ~ 0.65 V (Fig. 3.1-1b), ~ 0.80 V (Fig. 3.1-1c), ~ 0.98 V (Fig. 3.1-1d), corresponded to the reduction of bisphenolic cation radicals to their neutral forms.

The effective electropolymerization of poly(NiSalen)s was indicated by the appearance of anodic and cathodic waves, which increased in the following cycles. This observation demonstrates the initial electrochemical doping and the creation of charge transport species – bisphenolic radical cations within the conducting polymer layer deposited on the CP electrode.^{14,15,18} These waves were centered between 0.50 and 0.85 V for poly(NiSaltMe)s (Fig. 3.1-1a and b) and 0.50 – 0.75 V for poly(*meso*-NiSaldMe)-PD_{low} (Fig. 3.1-1c). However, due to the faster charge transfer, these waves were less pronounced for poly(*meso*-NiSaldMe)-PD_{high} (Fig. 3.1-1d). Moreover, the enhanced charge transport rate of poly(*meso*-NiSaldMe)-PD_{high} compared to poly(NiSaltMe)-PD_{high} was evident in the amount of charge passed within the same number of PD polymerization cycles. Charges passed during all PD electropolymerizations are summarized in Table 3.1-2.

Poly(NiSalen)s were also fabricated under PS conditions, resulting in the deposition of poly(NiSaltMe)-PS_{low}, poly(NiSaltMe)-PS_{high}, poly(*meso*-NiSaldMe)-PS_{low}, and poly(*meso*-NiSaldMe)-PS_{high} precursors. These precursors were deposited at a constant potential of 1.3 V vs. Ag/Ag⁺. This potential was necessary to enable the two-electron oxidation of NiSalen and

the subsequent two-electron transfer, leading to the continuous formation of a fully oxidized poly(NiSalen) during PS electrodeposition. The constant potential was maintained for a duration necessary to deposit a charge equivalent to that achieved during the electropolymerization under PD conditions, e.g., 877 s for poly(NiSaltMe)-PS_{low}, 1036 s for poly(NiSaltMe)-PS_{high}, 782 s for poly(*meso*-NiSaldMe)-PS_{low}, and 2107 s for poly(*meso*-NiSaldMe)-PS_{high}.

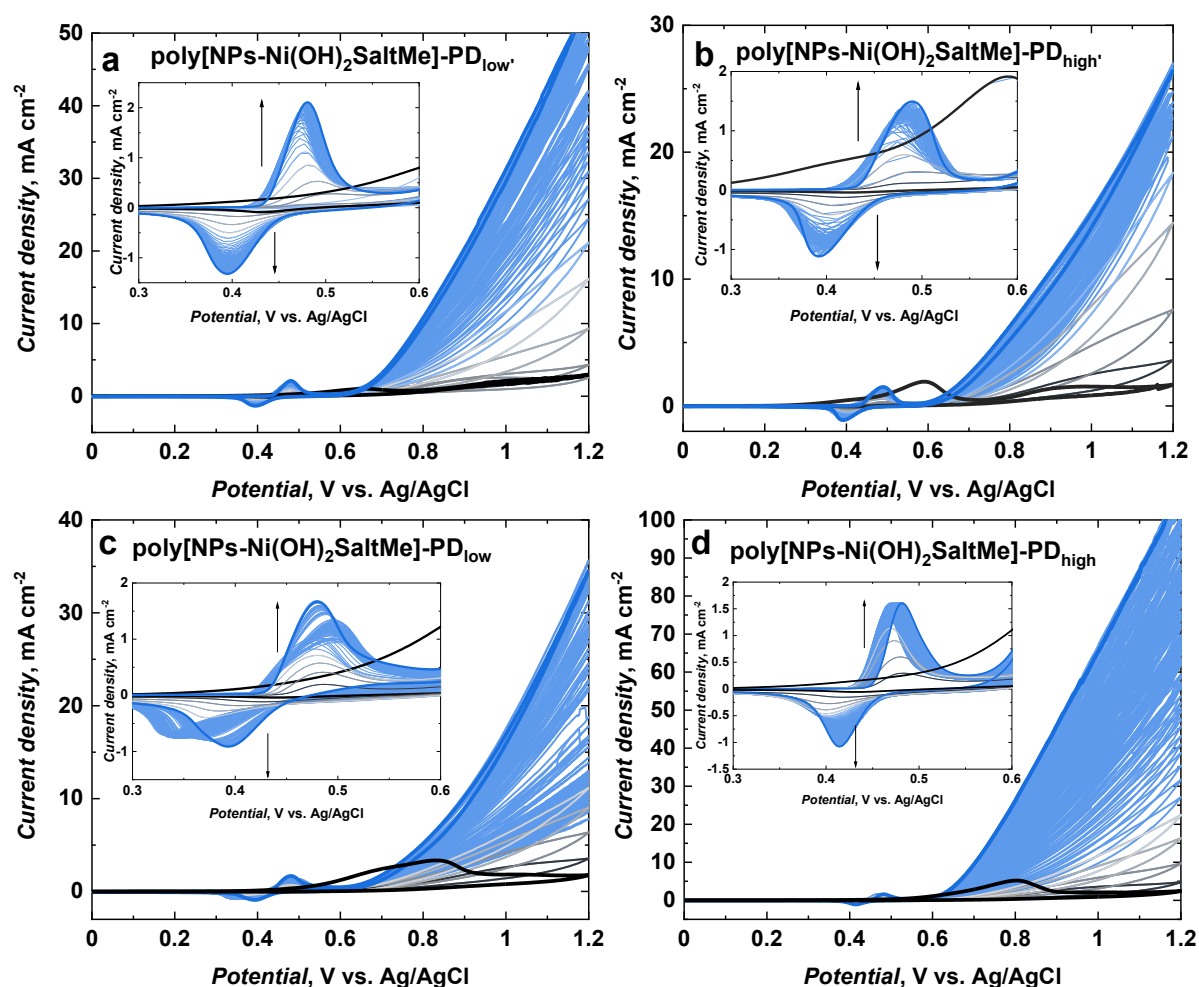
Table 3.1-2. Summary of the Ni(OH)₂-type NPs generation from differently deposited poly(NiSalen)s.

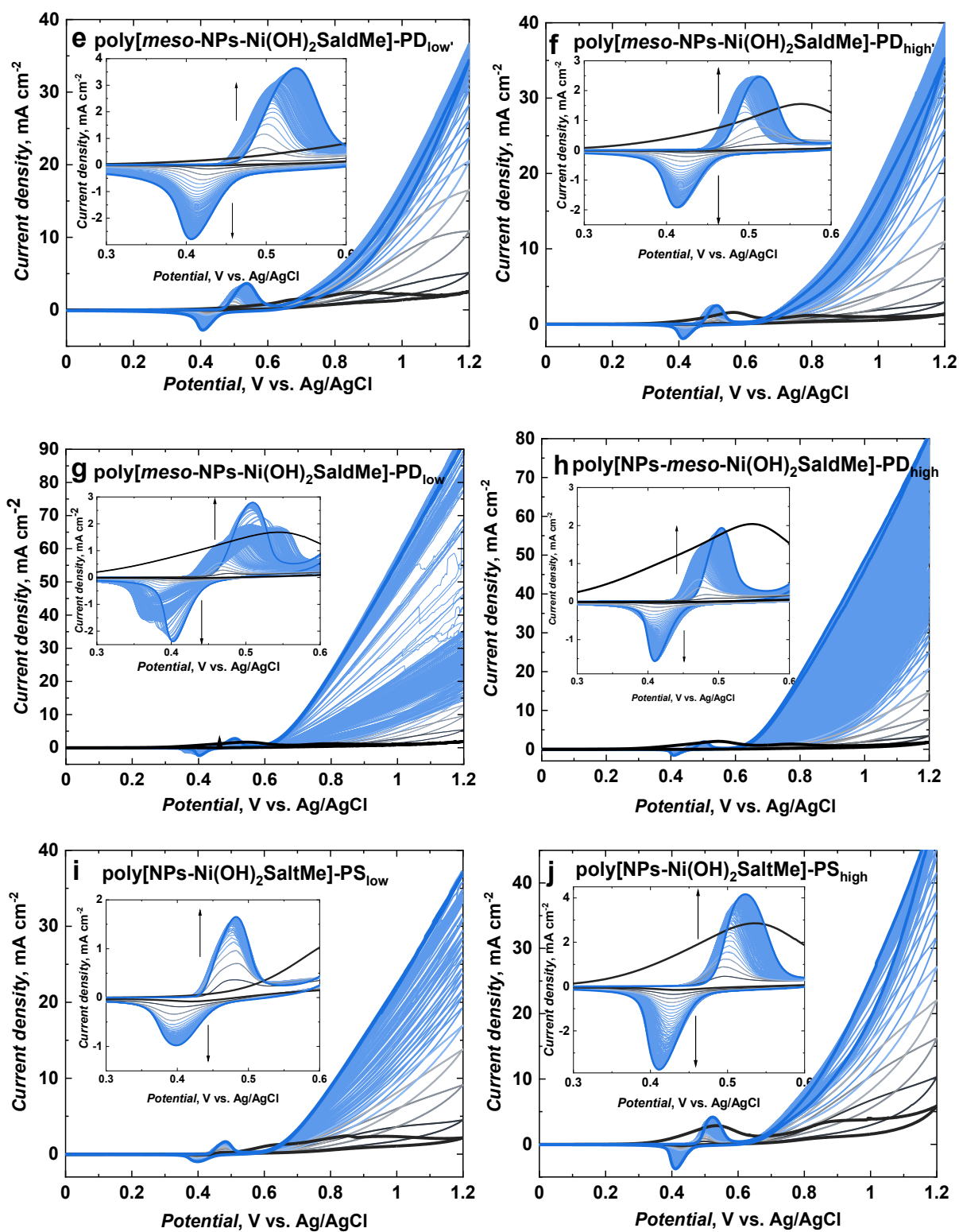
Electrodeposition conditions	Poly(NiSaltMe)		Poly(<i>meso</i> -NiSaldMe)	
	Charge (mC cm ⁻²)	Number of cycles for NPs generation	Charge (mC cm ⁻²)	Number of cycles for NPs generation
PD 2 mV s ⁻¹	83.3	120	117.3	280
PD' 2 mV s ⁻¹	51.3	55	69.3	150
PS	81.6	40	137.1	80
PD 100 mV s ⁻¹	181.1	130	178.5	250
PD' 100 mV s ⁻¹	88.2	62	94.3	120
PS	176.4	57	188.7	145

3.1.2 Potential-driven transformation of poly(NiSalen) precursors into poly[NPs-Ni(OH)₂Salen] catalysts: mechanistic elucidation

The potential-driven electrochemical transformation of all poly(NiSalen) precursors into Ni(OH)₂ NPs embedded in poly(Salen) matrix was conducted in 0.2 M NaOH_{aq} in the potential range of 0.0-1.2 V vs. Ag/AgCl with a scan rate of 20 mV s⁻¹. After the preparation step, polymer-coated CP electrodes were rinsed with Milli-Q water. This way six catalysts derived from poly(NiSaltMe) were prepared: poly[NPs-Ni(OH)₂SaltMe]-PD_{low}' (Fig. 3.1-2a), poly[NPs-Ni(OH)₂SaltMe]-PD_{high}' (Fig. 3.1-2b), poly[NPs-Ni(OH)₂SaltMe]-PD_{low} (Fig. 3.1-

2c), poly[NPs-Ni(OH)₂SaltMe]-PD_{high} (Fig. 3.1-2d) poly[NPs-Ni(OH)₂SaltMe]-PS_{low}, (Fig. 3.1-2i), and poly[NPs-Ni(OH)₂SaltMe]-PS_{high} (Fig. 3.1-2j) and six catalysts derived from poly(*meso*-NiSaldMe): poly[*meso*-NPs-Ni(OH)₂SaldMe]-PD_{low}, (Fig. 3.1-2e), poly[*meso*-NPs-Ni(OH)₂SaldMe]-PD_{high}, (Fig. 3.1-2f), poly[*meso*-NPs-Ni(OH)₂SaldMe]-PD_{low} (Fig. 3.1-2g), poly[*meso*-NPs-Ni(OH)₂SaldMe]-PD_{low}, (Fig. 3.1-2h), poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low}, (Fig. 3.1-2k), and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{high} (Fig. 3.1-2l). All further measurements for these catalysts were carried out in 0.2 M NaOH_{aq}.





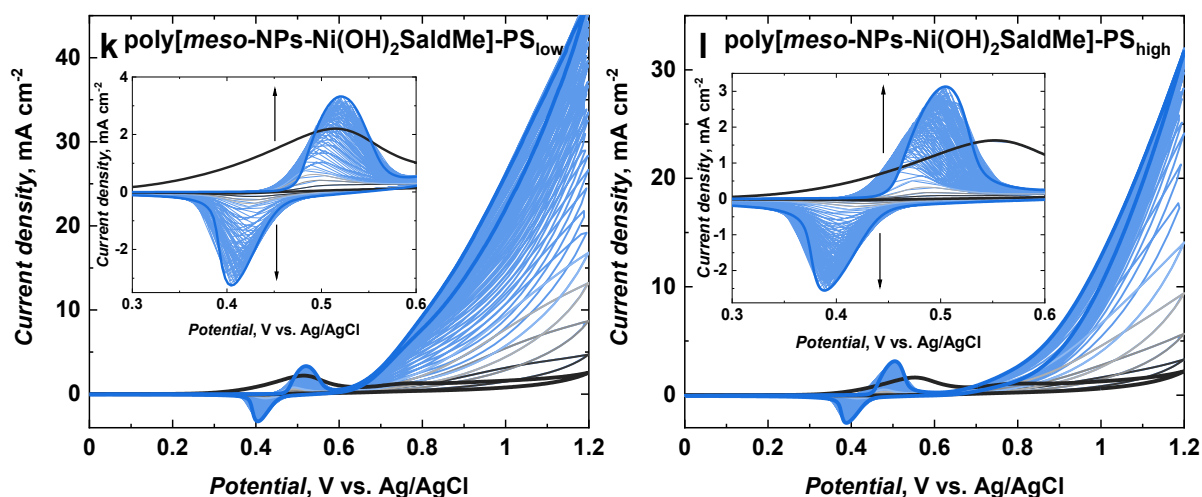
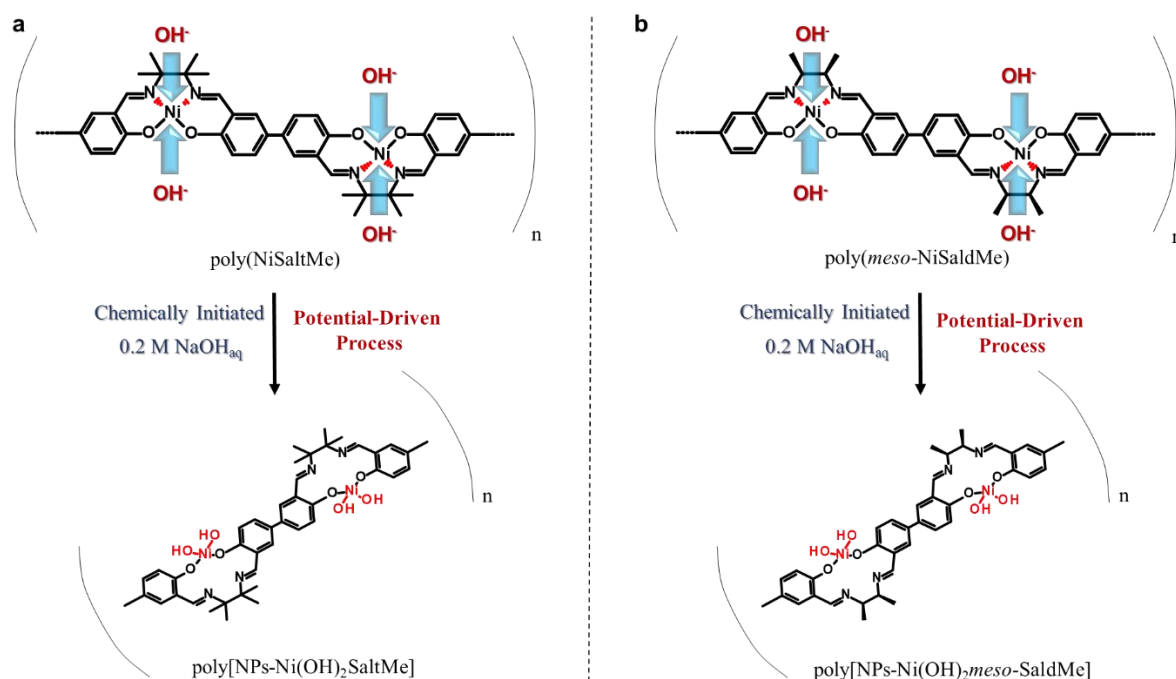


Figure 3.1-2. Multiple CV curves showing the potential-driven transformation of different (a, b, c, d, i, j) poly(NiSaltMe) and (e, f, g, h, k, l) poly(*meso*-NiSaldMe) precursors into poly[NPs-Ni(OH)₂Salen] catalysts. This transformation was carried out in 0.2 M NaOH_{aq} with a scan rate of 20 mV s⁻¹.

In the ACN solvent, poly(NiSalen) precursor behaves like polyphenylene, where the Ni center serves as a channel between the biphenylene moieties.⁵ In the presence of ED molecules capable of axially coordinating to the Ni²⁺ center, the primary target of electron release can be changed^{6,9,159} resulting in the electrooxidation of Ni²⁺ to Ni³⁺.^{9,159} The change of the primary site of electron release from the phenolic Salen center to the Ni center in alkaline media is identified as the electrochemically driven formation of poly[NPs-Ni(OH)₂Salen] (Scheme 3.1-1). After applying potential in a 0.2 M NaOH_{aq} solution, the formation of two bonds with hydroxyl groups occurs, leading to the cleavage of the weak bonds between Ni and nitrogen. This potential-driven transformation is defined as basic hydrolysis.¹⁶⁰



Scheme 3.1-1. Illustration showing the change of square planar geometry of Ni^{2+} in (a) poly(NiSaltMe) and (b) poly(*meso*-NiSaldMe) by an electrochemically driven process.

Figure 3.1-2 shows the multi-cyclic curves of the potential-driven transformations of poly(NiSalen) precursors into poly[NPs-Ni(OH)₂Salen] catalysts. During this electrotransformation in 0.2 M NaOH_{aq}, the place of electron release gradually changed from the phenolic Salen center to the Ni center, which indicates the deactivation of the poly(Salen) matrix in alkaline media. On these CV curves, one oxidation and one reduction peak centered at ~0.5 V for Ni^{2+} oxidation to Ni^{3+} and ~0.4 V for Ni^{3+} reduction to Ni^{2+} were visible, corresponding to the $\text{poly}[\text{NPs-Ni(OH)}_2\text{Salen}] \rightleftharpoons \text{poly}(\text{NPs-Ni}^{3+}\text{OOHSalen})$ electrode process. The increase in these peaks showed a successful transformation. The stabilization of the CV curve indicated that all Ni(OH)₂-type NPs centers were electrogenerated. The number of cycles needed to complete the transformation of each poly(NiSalen) into poly[NPs-Ni(OH)₂Salen] catalysts was presented in Table 3.1-2. The electrochemical transformation was significantly longer for poly(*meso*-NiSaldMe) precursors deposited under PS and PD conditions than for

poly(NiSaltMe) precursors, which can be explained by the higher electrochemical stability of poly(*meso*-NiSaldMe) in moderately ED media.¹³⁴

3.1.3 Morphological characterization of poly(NiSalen) precursors and poly[NPs-Ni(OH)₂Salen] catalysts.

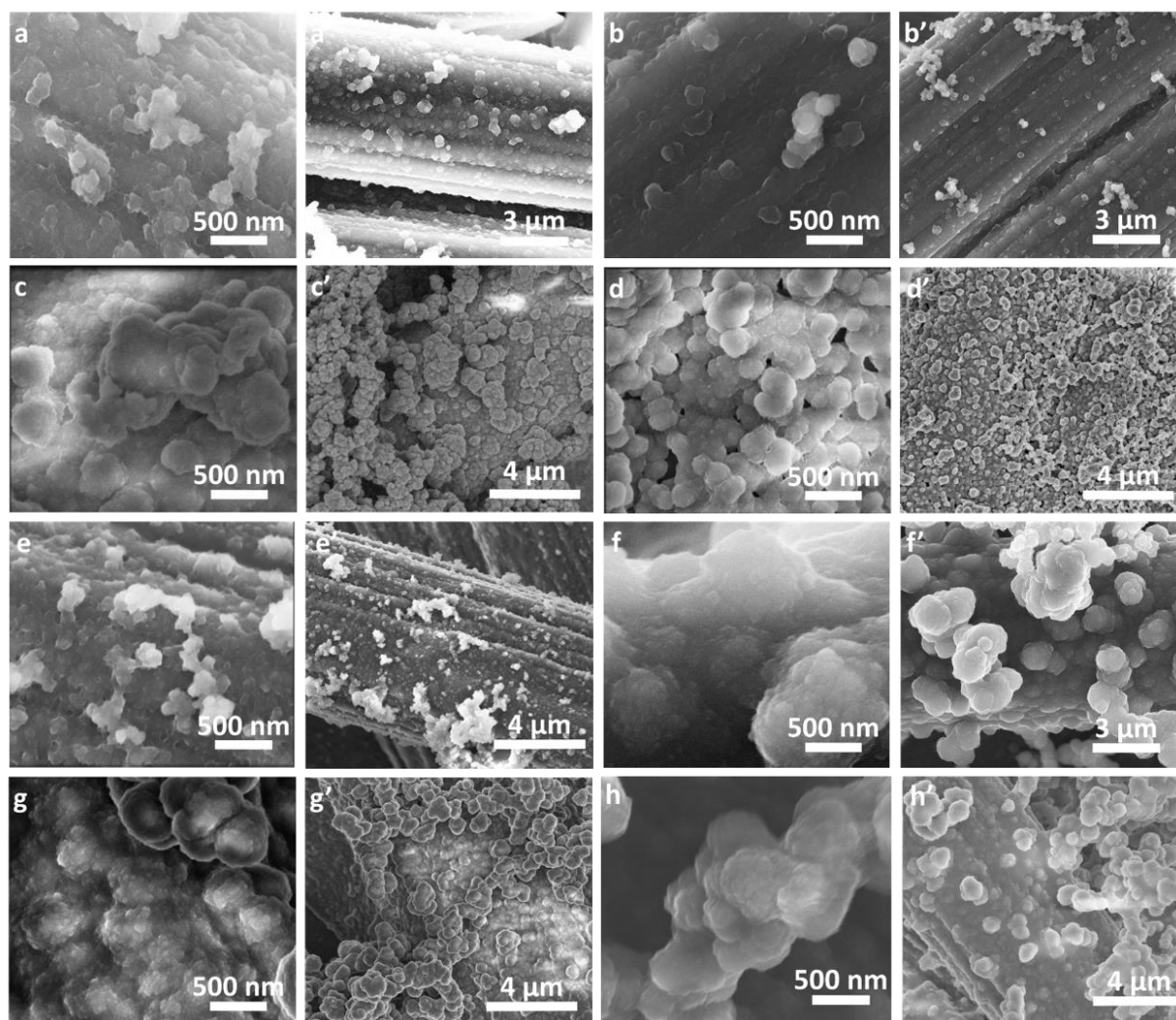


Figure 3.1-3. SEM images of poly(NiSalen) precursors presented at two magnifications: (a, a') poly(NiSaltMe)-PD_{low}, (b, b') poly(NiSaltMe)-PD_{high}, (c, c') poly(*meso*-NiSaldMe)-PD_{low}, (d, d') poly(*meso*-NiSaldMe)-PD_{high}, (e, e') poly(NiSaltMe)-PS_{low}, (f, f') poly(NiSaltMe)-PS_{high}, (g, g') poly(*meso*-NiSaldMe)-PS_{low}, (h, h') poly(*meso*-NiSaldMe)-PS_{high},

The poly(NiSalen)s deposited on the CP electrode under PD and PS conditions were imaged with the SEM (Figure 3.1-3). The polymer completely covered the CP electrode fibers. The morphology of the deposited precursors was influenced by the conditions applied during electropolymerization. The poly(NiSaltMe)-PD_{low}' (Fig. 3.1-3a, a') and poly(NiSaltMe)-PD_{high}' (Fig. 3.1-3b, b') appeared relatively flat and uniform, with characteristic sporadic bubble-shaped structures. The poly(NiSaltMe)-PS_{low} (Fig. 3.1-3e, e') exhibited a similar structure but with a slightly more irregular morphology. In contrast, the poly(NiSaltMe)-PS_{high} (Fig. 3.1-3f, f') revealed a spatially diversified globular structure, the most pronounced among all poly(NiSaltMe) precursors.

All poly(*meso*-NiSaldMe) precursors displayed a spatially diversified structure with globular shapes. The poly(*meso*-NiSaldMe)-PD_{low}' (Fig. 3.1-3c, c') was composed of irregular globules, while poly(*meso*-NiSaldMe)-PD_{high}' (Fig. 3.1-3d, d') featured more regular globules. Both poly(*meso*-NiSaldMe)-PS_{low} (Fig. 3.1-3g, g') and poly(*meso*-NiSaldMe)-PS_{high} (Fig. 3.1-3h, h') exhibited densely packed structures with spatially diversified globular formations, resembling cauliflower-like structures.

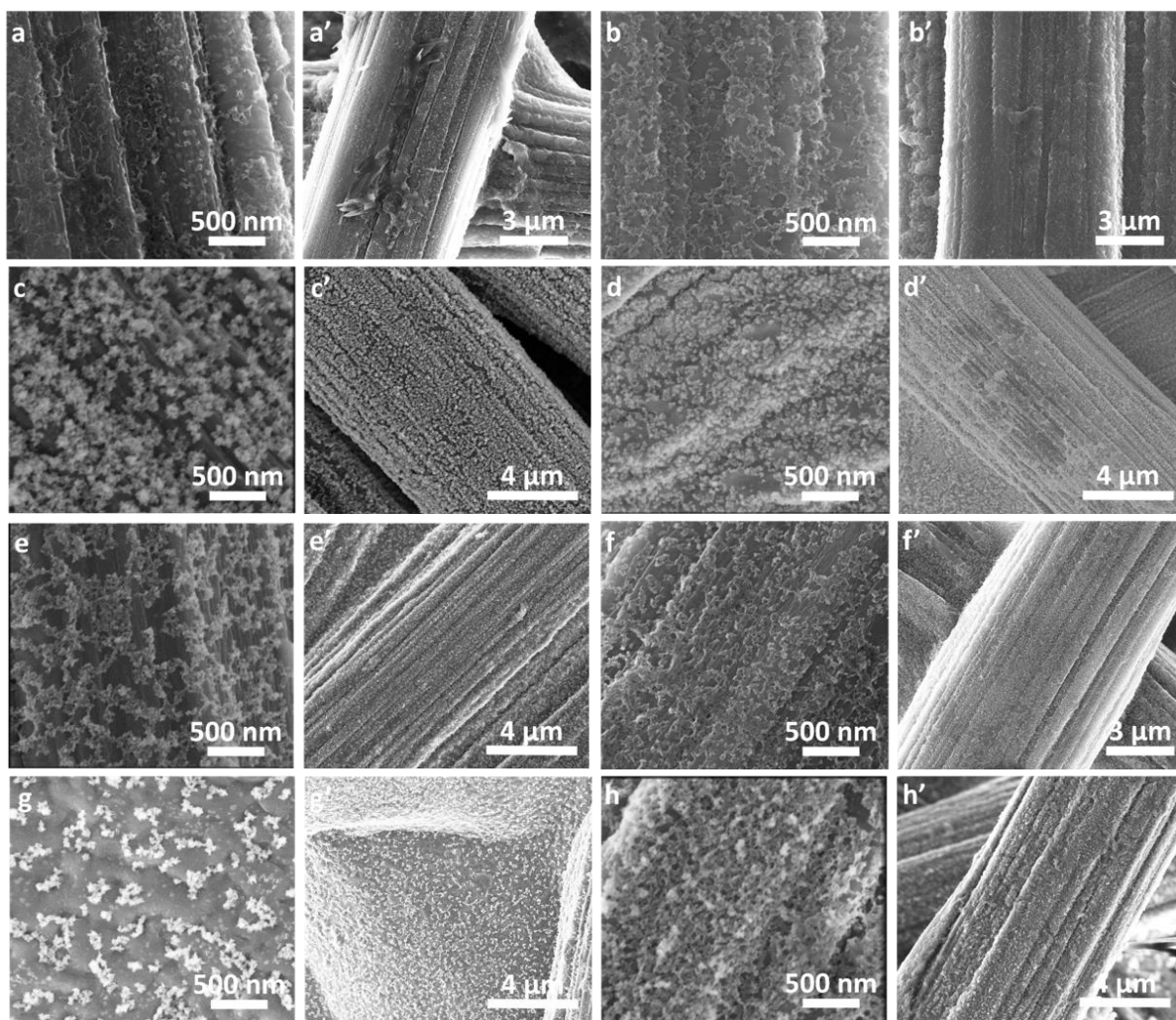


Figure 3.1-4. SEM images of (a, a') poly[NPs-Ni(OH)₂SaltMe]-PD_{low}', (b, b') poly[NPs-Ni(OH)₂SaltMe]-PD_{high}', (c, c') poly[*meso*-NPs-Ni(OH)₂SaldMe]-PD_{low}', (d, d') poly[*meso*-NPs-Ni(OH)₂SaldMe]-PD_{high}', (e, e') poly[NPs-Ni(OH)₂SaltMe]-PS_{low}, (f, f') poly[NPs-Ni(OH)₂SaltMe]-PS_{high}, (g, g') poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low}, and (h, h') poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{high} prepared from different poly(NiSalen)s prepared under different electrodeposition conditions.

The SEM images of the poly[NPs-Ni(OH)₂Salen] catalysts prepared from different poly(NiSalen)s deposited under various conditions are presented in Figure 3.1-4. These catalysts did not cover the CP fibers, but they did show an even distribution across the fibers. The morphology of the poly(NiSalen) precursors significantly influenced the structure of the generated catalysts. The flat and relatively homogenous poly(NiSaltMe) precursors led to a 2D

arrangement of poly(SaltMe) matrix, within which Ni(OH)₂ NPs were embedded (Fig. 3.1-4a, a', b, b', e, and e'). However, the globular poly(NiSaltMe)-PS_{high} (Fig. 3.1-4f, f') resulted in the most spatially diversified matrix arrangement among poly(SaltMe) matrices. On the other hand, the globular structure of poly(*meso*-NiSaldMe) precursors facilitated the 3D templating of the Ni(OH)₂ NPs in the poly(*meso*-SaldMe) matrix (Fig. 3.1-4c, c', d, d', g, g', h, and h'). It was evident that the morphology of the poly(NiSalen) precursor governed the spatial arrangement of the matrix and NPs embedded in it.

3.1.4 Electrocatalytic performance of the poly[NPs-Ni(OH)₂Salen] catalyst

Figures 3.1-5 and 3.1-6 present the catalytic CV responses of the poly[NPs-Ni(OH)₂SaltMe] and poly(*meso*-NPs-Ni(OH)₂SaldMe] catalysts, respectively, in the absence (black curves) and presence of the ethanol concentrations ranging from 0.05 to 1.0 M. With each addition of ethanol, an increase in the anodic current density was observed, accompanied by a decrease in the cathodic peak during the backward scan. The current increase in the forward scan is due to the electrooxidation of ethanol, which occurs at a potential close to that for NiOOH formation. The catalytic peak was followed by a peak corresponding to the oxygen evolution reaction (OER).¹⁶¹

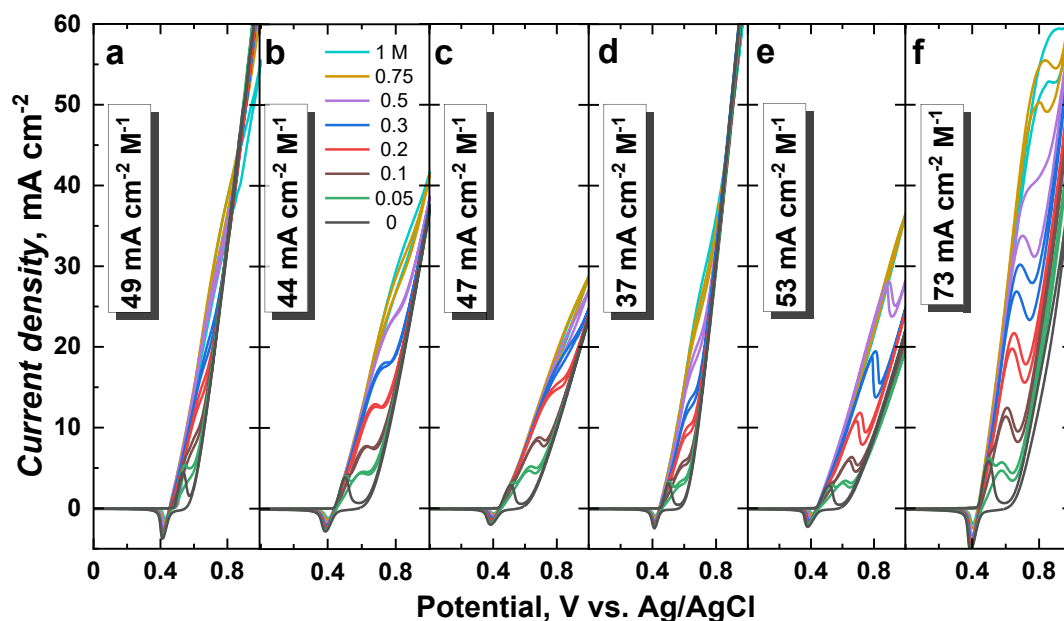


Figure 3.1-5. Catalytic CV responses of (a) poly[NPs-Ni(OH)₂SaltMe]-PD_{low}, (b) poly[NPs-Ni(OH)₂SaltMe]-PD_{low}', (c) poly[NPs-Ni(OH)₂SaltMe]-PS_{low}, (d) poly[NPs-Ni(OH)₂SaltMe]-PD_{high}, (e) poly[NPs-Ni(OH)₂SaltMe]-PD_{high}', and (f) poly[NPs-Ni(OH)₂SaltMe]-PS_{high}, toward different ethanol concentrations. The CVs were measured in 0.2 M NaOH_{aq} at 50 mV s⁻¹. The corresponding sensitivity values are displayed as insets for each catalyst.

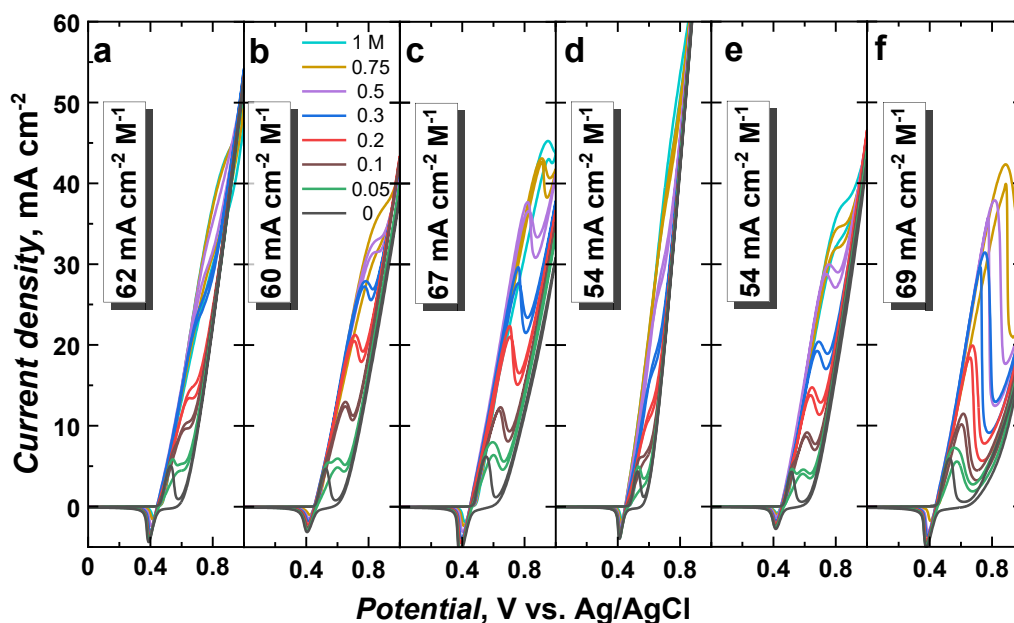


Figure 3.1-6. Catalytic CV responses of (a) poly[*meso*-NPs-Ni(OH)₂SaldMe]-PD_{low} (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]-PD_{low}', (c) poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low}, (d) poly[*meso*-NPs-Ni(OH)₂SaldMe]-PD_{high} (e) poly[*meso*-NPs-Ni(OH)₂SaldMe]-PD_{high}', and (f) poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{high}, toward different ethanol concentrations. The CVs were measured in 0.2 M NaOH_{aq} at 50 mV s⁻¹. The corresponding sensitivity values are displayed as insets for each catalyst.

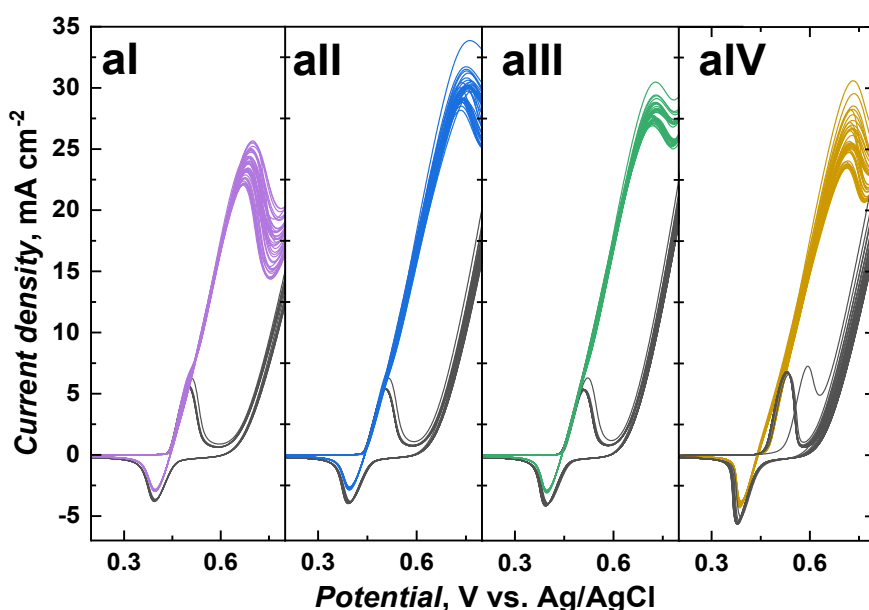
The catalytic performance of the poly[NPs-Ni(OH)₂Salen] catalysts was found to be closely related to the morphologies of their poly(NiSalen) precursors. When the Ni(OH)₂ NPs were embedded in a relatively flat poly(SaltMe) matrix, their catalytic responses were low (Figure 3.1-5). Among all poly[NPs-Ni(OH)₂SaltMe] catalysts, the highest catalytic current was obtained for poly[NPs-Ni(OH)₂SaltMe]-PS_{high} (Figure 3.1-5f), derived from the poly(NiSaltMe)-PS_{high} precursor with the most spatially diversified structure. In contrast, the catalytic currents were higher when Ni(OH)₂ NPs were templated in a 3D poly(*meso*-SaldMe) matrix (Fig. 3.1-6). Moreover, the catalytic peak potential was shifted only ~370 mV from its initial Ni²⁺/Ni³⁺ oxidation potential (Fig. 3.1-6), which is lower compared to the shift of the ~500 mV observed for poly[NPs-Ni(OH)₂SaltMe] catalysts (Fig. 3.1-5).

All poly[NPs-Ni(OH)₂Salen] catalysts exhibited a linear increase in electrocatalytic current toward ethanol electrooxidation in a concentration range of 0.05 – 0.5 M. At higher concentrations, a deviation from linearity was observed, suggesting the occurrence of saturation of the catalytic activity. The catalytic efficiencies obtained for all catalysts are shown above, in the catalytic results (Fig. 3.1-5 and 3.1-6). The product of ethanol electrooxidation was acetic acid (CH₃COOH).¹⁶² The highest electrochemical responses were obtained for poly[NPs-Ni(OH)₂SaltMe]-PS_{high} (Fig. 3.1-5f) and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} (Fig. 3.1-6c). Even though a lower polymer mass was deposited during the PS_{low} condition, compared to PS_{high}, the electrocatalytic activity was similar. Keeping all these points in mind, Ni(OH)₂-type

NPs derived from poly(NiSaltMe)-PS_{high} and poly(*meso*-NiSaldMe)-PS_{low} were selected for further study.

3.1.5 Catalytic activity stability

The stability and the regeneration ability of the poly[NPs-Ni(OH)₂Salen] catalysts were examined through a multi-cyclic catalytic experiment in a solution of 0.2 M NaOH_{aq} and 0.3 M ethanol (Fig. 3.1-7). The 20 electrocatalytic cycles were measured on the freshly prepared electrodes (Fig. 3.1-7aI, bI), after immediate regeneration (Fig. 3.1-7aII, bII), the following day (Fig. 3.1-7aIII, bIII), and after ten days (Fig. 3.1-7aIV, bIV). The steady magnitude of the catalytic currents over time indicated that the catalysts remained stable, confirming that their active sites were not blocked by electrooxidation intermediates/products, and that multiple regenerations of these catalysts were feasible. The currents during the multiple CV cycles (20 cycles) remained similar due to catalyst regeneration during the reverse scan, preventing the adsorption of ethanol oxidation intermediates/products.



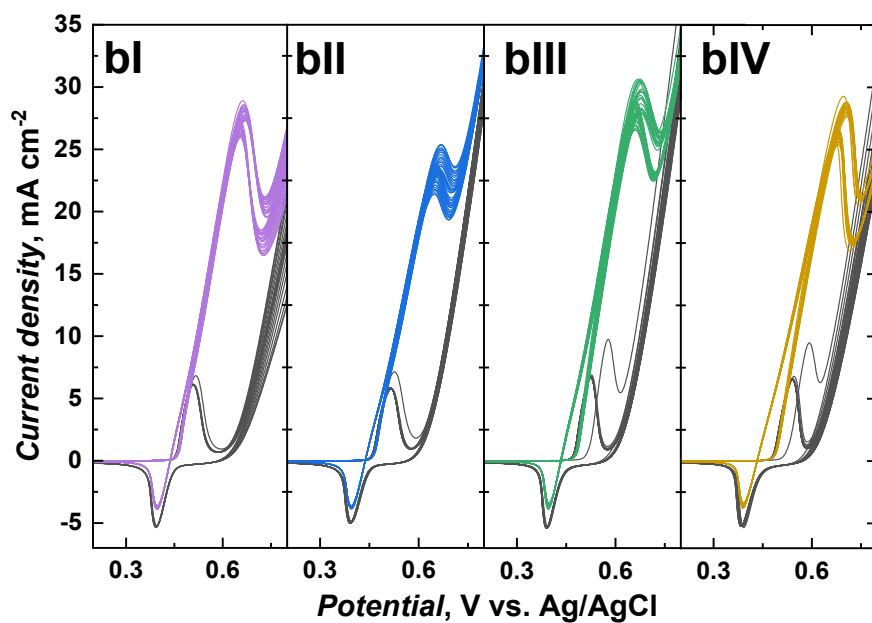


Figure 3.1-7. Multiple CV measured for (I) freshly electrogenerated and (II-IV) regenerated (a) poly[NPs-Ni(OH)₂SaltMe]-PS_{high} and (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} using a scan rate of 50 mV s⁻¹ in 0.2 M NaOH_{aq} in the presence of 0.3 M ethanol.

3.1.6 TEM images of poly[NPs-Ni(OH)₂Salen]-PS_{high} and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalysts

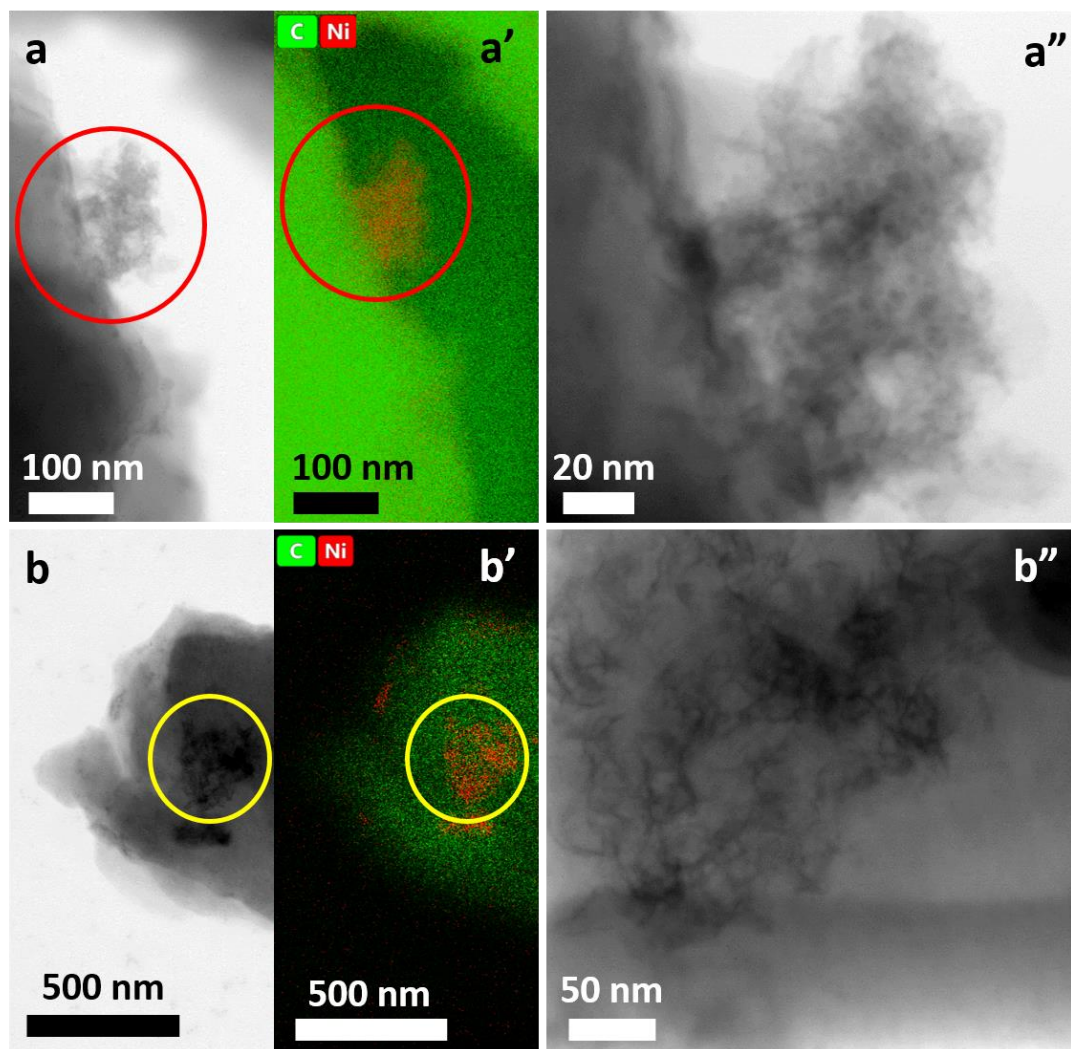


Figure 3.1-8. TEM images (a, a'' b, and b'') and EDX mapping (a' and b') of (a, a' a'') poly[NPs-Ni(OH)₂SaltMe]-PS_{high}, and (b, b', b'') poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low}.

The EDX element profiling (Fig. 3.1-8a' and b') confirmed the presence of carbon (C), and Ni in the catalyst, proving the presence of the Ni(OH)₂ NPs embedded within the poly(Salen) matrices. This element profiling indicated that the distances between Ni(OH)₂ NPs were larger for poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low}, suggesting that active sites are more spatially

distributed in this catalyst. Figure 3.1-8a'' and b'' showed a magnified view of the circled area in Figure 3.1-8a and b. This highlighted the spatial distribution of poly(Salen) matrices, which determined the arrangement of Ni(OH)₂ NPs. A more extensive spatial distribution was visible for the poly(*meso*-SaldMe) matrix. Ni(OH)₂ NPs embedded within this non-conductive matrix (in aqueous strong donor media) prevented the permanent adsorption of counter-ions during doping and dedoping, as well as the substrate and product of the electrocatalytic reaction.

3.1.7 X-ray photoelectron spectroscopy characterization of the poly(NiSalen) precursors and poly[NPs-Ni(OH)₂Salen] catalysts

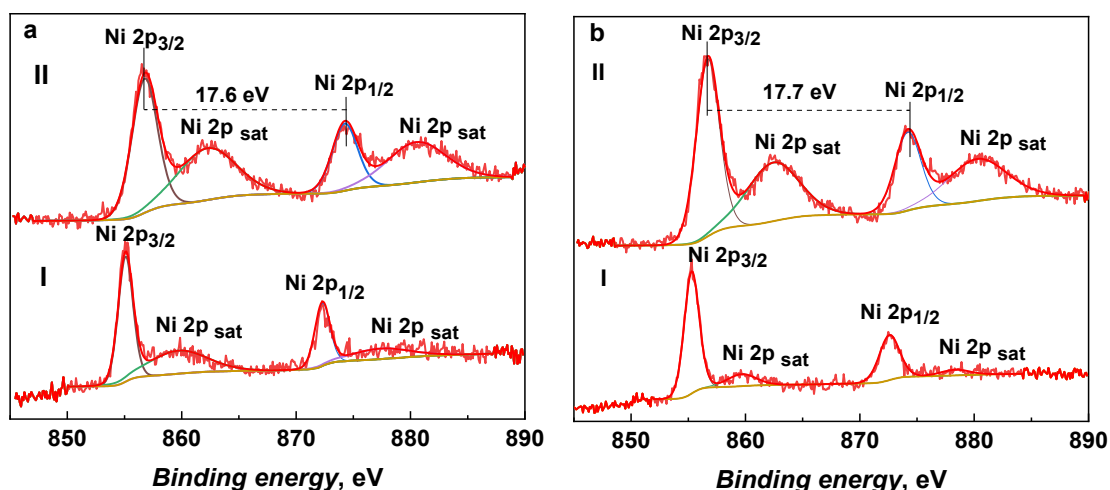


Figure 3.1-9. Ni 2p XPS spectra of (a I) poly(*meso*-NiSaldMe)-PS_{low}, (a II) poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low}, (b I) poly(NiSaltMe)-PS_{high} and (b II) poly[NPs-Ni(OH)₂SaltMe]-PS_{high}.

Using XPS, the chemical nature of Ni²⁺ species in poly(NiSalen) precursors and poly[NPs-Ni(OH)₂Salen] catalysts was characterized and presented in Figure 3.1-9. The binding energies of the Ni 2p_{3/2} and Ni 2p_{1/2} for poly[NPs-Ni(OH)₂SaltMe]-PS_{high} (Fig. 3.1-9bII) and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} (Fig. 3.1-9aII) were ~856 and ~874 eV, respectively. The difference between these binding energies was approximately 17.6 eV, confirming the presence

of Ni(OH)₂ NPs.^{163,164} Furthermore, the presence of Ni 2p satellite peaks indicated the existence of a high-spin divalent state of Ni²⁺ in the poly[NPs-Ni(OH)₂Salen] catalysts and confirmed the loss of square-planar geometry of Ni²⁺.¹⁶⁵ The obtained binding energies were slightly different in poly(NiSalen)s and Ni(OH)₂-based NPs catalysts. The Ni 2p_{3/2} binding energy was shifted from ~855 to ~856 eV, whereas the Ni 2p_{1/2} binding energy was shifted from ~872 to ~874 eV from polymer precursor samples to catalyst samples.

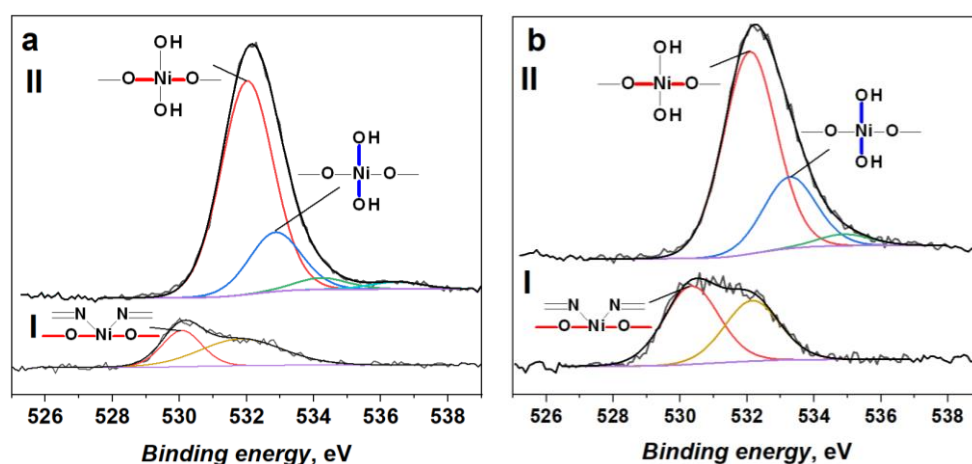


Figure 3.1-10. O 1s XPS spectra of (a I) poly(NiSaltMe)-PS_{high} and (a II) poly[NPs-Ni(OH)₂SaltMe]-PS_{high}, (b I) poly(*meso*-NiSaldMe)-PS_{low} and (b II) poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low}.

Additionally, the O 1s spectra of polymer precursors are presented in Figure 3.1-10aI for poly(NiSaltMe)-PS_{high} and Figure 3.1-10bI for poly(*meso*-NiSaldMe)-PS_{low}. The peak observed for 530.2 eV corresponded to the C-O-Ni oxygen atom.¹⁶⁶ Figures 3.1-10aII and 3.1-10bII presented the O 1s spectra for poly[NPs-Ni(OH)₂SaltMe]-PS_{high} and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low}, respectively. These spectra exhibited two peaks at 532.1 and 533.3 eV binding energies, corresponding to Ni-O and OH⁻ from Ni(OH)₂, respectively.¹⁶⁷ Thus, it confirmed that OH⁻ groups coordinated to the Ni center during the potential-driven generation process.

3.1.8 Confirmation of stability of poly[NPs-Ni(OH)₂NiSaldMe]-PS_{high}, and poly[*meso*-NPs-Ni(OH)₂NiSaldMe]-PS_{low} catalysts

The XPS spectra after the ethanol electrooxidation and before are shown in Figures 3.1-11 a, and b. The binding energies of the Ni 2p_{1/2} and Ni 2p_{3/2} peaks are in similar positions as for the freshly prepared poly[NPs-Ni(OH)₂Salen] catalyst. The Ni 2p spectra after ethanol electrooxidation exhibit the binding energies of Ni 2p_{3/2} and Ni 2p_{1/2} at ~857.0 and ~874.6 eV for poly[NPs-Ni(OH)₂SaltMe]-PS_{high}, derived catalyst, and ~856.3 and ~874.0 eV poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalyst.

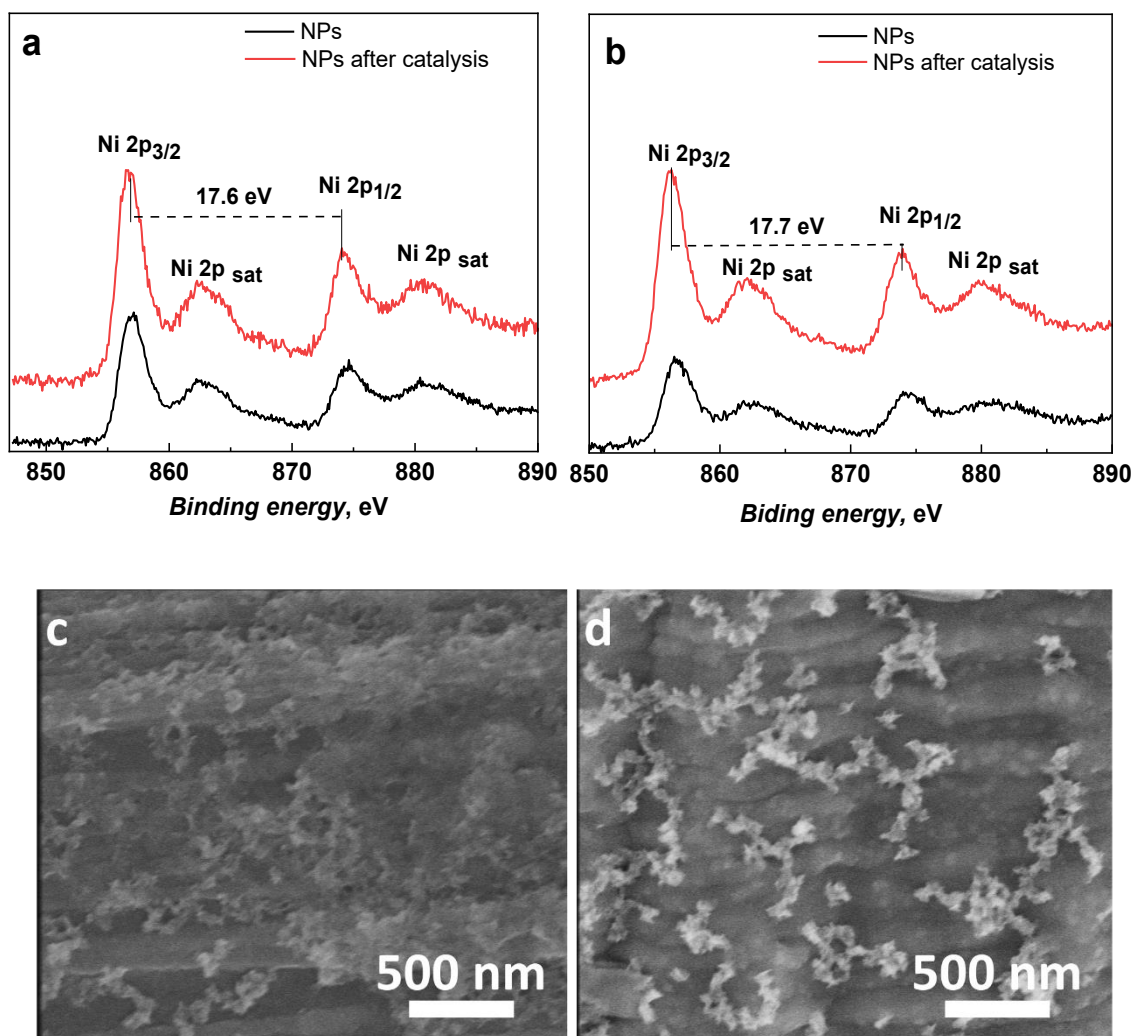


Figure 3.1-11. (a, b) Ni 2p XPS spectra, before (black) and after (red) catalytic electrooxidation of ethanol on (a) poly[NPs-Ni(OH)₂SaltMe]-PS_{high}, and (b) poly[*meso*-NPs-

Ni(OH)₂SaldMe]-PS_{low}. SEM images of (c) poly[NPs-Ni(OH)₂SaltMe]-PS_{high}, and (d) poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} after ethanol electrooxidation.

No visible change in SEM morphologies (Fig. 3.1-11c and d) and XPS spectra (Fig. 3.1-11a and b) supported that NPs derived from poly(*meso*-NiSaldMe) and poly(NiSaltMe) are resistant to poisoning effects and can be used multiple times.

3.1.9 Electrochemical characterization of poly[NPs-Ni(OH)₂Salen]-PS_{high} and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalysts

The multiple-scan rate and constant-potential EIS experiments were conducted in the presence and absence of ethanol for two catalysts: poly[NPs-Ni(OH)₂SaltMe]-PS_{high} and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low}. These two materials showed the best electrocatalytic performance (Fig. 3.1-5f and 3.1-6c). These studies were performed to examine charge transfer occurring at the CP electrode | poly[NPs-Ni(OH)₂Salen] interface and associated mass transport processes. For that, CV responses were registered at scan rates of 2, 5, 10, 30, 50, 100, and 200 mV s⁻¹ in the 0.2 M NaOH_{aq}.

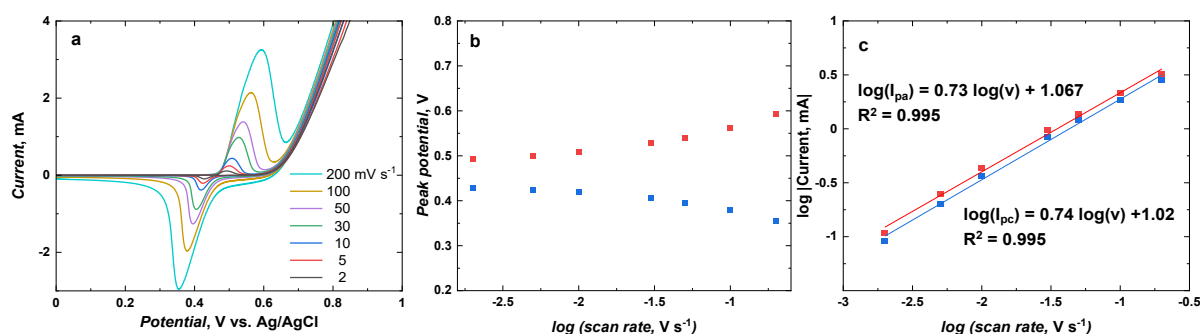


Figure 3.1-12. (a) CV curves of poly[NPs-Ni(OH)₂SaltMe]-PS_{high} performed at different scan rates in 0.2 M NaOH_{aq}. (b) The anodic (red curve) and cathodic (blue curve) peak potentials vs. the logarithm of the scan rate. (c) The logarithm of the anodic (red curve) and cathodic (blue curve) peak current dependence on the logarithm of the scan rate.

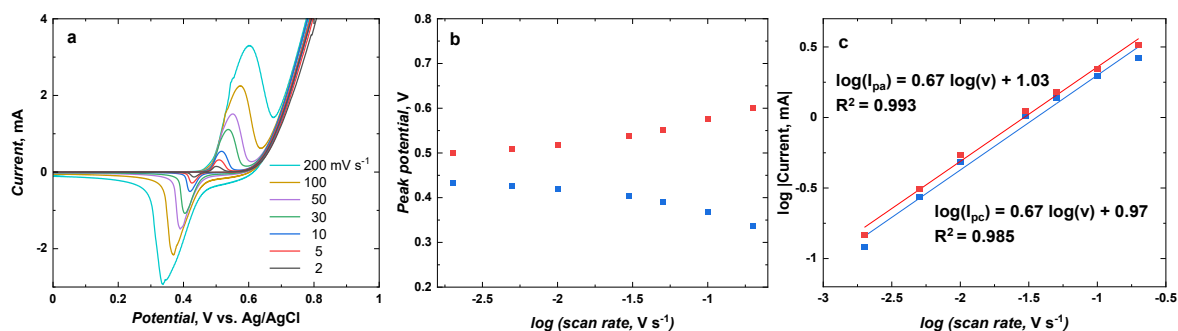


Figure 3.1-13. (a) CV curves of poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} performed at different scan rates in 0.2 M NaOH_{aq}. (b) The anodic (red curve) and cathodic (blue curve) peak potentials vs. the logarithm of the scan rate. (c) The logarithm of the anodic (red curve) and cathodic (blue curve) peak current dependence on the logarithm of the scan rate.

The multiple scan rates responses of a poly[NPs-Ni(OH)₂SaltMe]-PS_{high} (Fig. 3.1-12a) and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} (Fig. 3.1-13a) catalysts revealed a single anodic and cathodic peak, indicating that the Ni²⁺/Ni³⁺ oxidation/reduction is a one-electron process. Redox-active materials intended for electrocatalytic application must exhibit electrochemical behavior governed by fast charge transfer in the supporting electrolyte solution. Charge transfer becomes the rate-determining step when electron transport within the electroactive species confined to the electrode surface is slower than mass transport, and the redox equilibrium does not prevail. In a multiple-scan-rate experiment, kinetic control of the electrochemical charge-transport process typically results in a proportional increase in the anodic and cathodic peak-to-peak separation, along with a decrease in peak current.^{168,169} This behavior was not observed for poly[NPs-Ni(OH)₂SaltMe]-PS_{high} (Fig. 3.1-12a) and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} (Fig. 3.1-13a) catalysts, indicating that the kinetics of faradaic charge-transfer processes within these catalyst materials were fast.

The peak potential separation of poly[NPs-Ni²⁺(OH)₂Salen] $\rightleftharpoons$ poly(NPs-Ni³⁺OOHSalen) processes remained stable up to 10 mV s⁻¹ for both catalysts (Fig. 3.1-12b and 3.1-13 b). At higher scan rates, an increase in the anodic and cathodic peak separation was observed. This

separation was more pronounced for poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} (Fig. 3.1-13b) because of the non-conducting spatially diversified poly(*meso*-SaldMe) matrix, which induced ohmic resistance. Moreover, the peaks for poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} were broader than those for poly[NPs-Ni(OH)₂SaltMe]-PS_{high}, indicating repulsive interaction between electroactive species embedded in the poly(*meso*-SaldMe) matrix.^{140,170} Additionally, the redox equilibrium prevailed for both catalysts, indicating reversibility in both processes.¹⁴⁰ In Figure 3.1-12 c, the dependence of the logarithm of the anodic and cathodic peak currents on the logarithm of the scan rate was presented. The slopes of these dependencies are 0.73 and 0.74 for the anodic and cathodic curves, respectively, for poly[NPs-Ni(OH)₂SaltMe]-PS_{high} catalyst. This observation suggested that the oxidation and reduction processes were under finite diffusion control.^{142,143} Indicating that the thickness of the poly[NPs-Ni(OH)₂SaltMe]-PS_{high} catalyst was lower than or equal to the thickness of the diffusion layer at the studied scan rates. However, the start of changes in the peak potential at scan rates above 50 mV s⁻¹ suggests the beginning of a change from a thin-layer regime to semi-infinite diffusion control.^{142,143} This slope of log(*I*) vs. log(*v*) dependence for poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} (Fig. 3.1-13c) was 0.67 for both oxidation and reduction peak currents, suggesting that these processes were close to entering semi-infinite diffusion control. The analysis described above confirmed that the oxidation/reduction processes of poly[NPs-Ni(OH)₂SaltMe]-PS_{high} and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalysts were fast and under diffusion control.

Area accessible for counterions (*A_{CI}*) was calculated to gain deeper insights into observed differences in the electrochemical behavior of poly[NPs-Ni(OH)₂SaltMe]-PS_{high} (Fig. 3.1-12a) and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} (Fig. 3.1-13a) catalysts. Moreover, it helped establish the influence of poly(Salen) matrix morphology on the catalytic performance of Ni(OH)₂-type NPs. *A_{CI}* value describes the development of the catalyst surface in reference to the geometric area. The *A_{CI}* values were calculated according to Equation 3.1-1.

$$A_{CI} = \frac{C_{CP}}{C_S}, \quad \text{where } C_{CP} = \frac{\int_{V_1}^{V_2} I(t) dV}{\Delta V}, \quad \text{and} \quad C_S = \frac{\int_{V_1}^{V_2} I(t) dV}{\Delta V A} \quad (3.1-1)$$

Where C_{CP} was the capacitance of the CP electrode, and C_S was the specific capacitance (capacitance determined from discharging part of the CV curves divided by geometric electrode area, A). The summary of the A_{CI} values obtained for various scan rates is presented in Table 3.1-3.

Table 3.1-3. A_{CI} values determined from the multi-scan rate experiment conducted for poly[NPs-Ni(OH)₂Salen] catalysts in 0.2 M NaOH_{aq}.

ν (mV s ⁻¹)	A_{CI} (cm ²)	
	Poly[NPs-Ni(OH) ₂ SaltMe]-PS _{high}	Poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe]-PS _{low}
2	0.180	0.197
5	0.150	0.164
10	0.128	0.146
30	0.057	0.064
50	0.036	0.041
100	0.019	0.021
200	0.010	0.011

Poly[NPs-Ni(OH)₂Salen] catalysts were characterized by diffusion-controlled oxidation and reduction Ni²⁺/Ni³⁺ processes, as reflected in the calculated A_{CI} values (Table 3.1-3). The obtained A_{CI} values were lowest at the highest scan rates because the diffusion of OH⁻ counterions could not keep the rate of charge transfer of Ni²⁺ ⇌ Ni³⁺ for higher scan rates. The A_{CI} values were higher for the poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalyst, which explains its better catalytic performance and suggests that OH⁻ counterion diffusion in the poly[NPs-Ni(OH)₂SaltMe]-PS_{high} catalyst was hindered. This behavior can be attributed to the more spatially diversified 3D structure of the poly(*meso*-SaldMe) matrix, which favored this electrocatalytic behavior.

The EIS experiment was used to investigate the rate of charge-transfer processes taking place at the CP electrode | poly[NPs-Ni(OH)₂Salen] interface for both catalysts. The potentials 0.6 V and 0.65 V vs. Ag/AgCl were chosen for analysis because they corresponded to the electrogeneration of poly(NPs-Ni³⁺OOHSalen) active sites (Fig. 3.1-14).

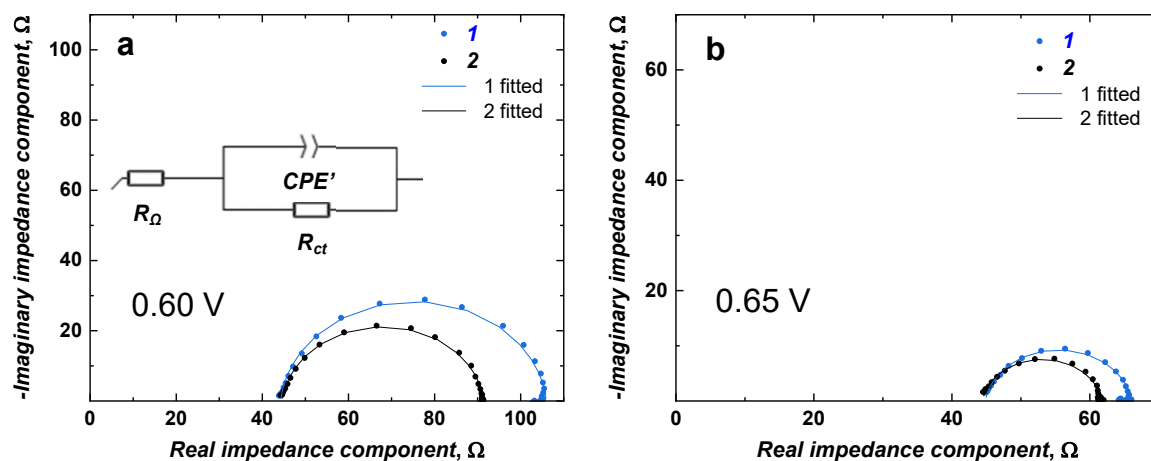


Figure 3.1-14. Comparative Nyquist plots for (1) poly[NPs-Ni(OH)₂SaltMe]-PS_{high}, and (2) poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low}. EIS measurements were registered in 0.2 M NaOH_{aq}, for constant potentials of (a) 0.60, and (b) 0.65 V. Inset: a modified Randles-Ershler equivalent electric circuit composed of R_{Ω} (ohmic resistance), CPE' (constant phase element), and R_{ct} (charge transfer resistance) electrical elements, used for fitting of the individual electrical circuit elements to the experimental data. The obtained impedance data were fitted to the Randles-Ershler equivalent circuit, composed of R_{Ω} , CPE' , and R_{ct} components (Table 3.1-4).

Calculated R_{ct} values at 0.6 and 0.65 V vs. Ag/AgCl were higher for poly[NPs-Ni(OH)₂SaltMe]-PS_{high}, while the C_{dl} values (calculated according to Equation 2.3-14) were higher for poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} (Table 3.1-4). This indicated that the charge transfer was faster for poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalyst under the specified conditions. Moreover, this finding confirmed the effective distribution of Ni(OH)₂ NPs within the poly(*meso*-SaldMe) matrix, facilitating faster and more efficient charge transfer.

Table 3.1-4. Summarization of the circuit elements' values obtained by fitting EIS experimental data.

Ethanol concentration (M)	Potential (V)	Poly[NPs-Ni(OH) ₂ SaltMe]				Poly[<i>meso</i> -NPs-Ni(OH) ₂ NiSaldMe]			
		R_{Ω} (Ω)	R_{ct} (Ω)	C_{dl} (mF)	p	R_{Ω} (Ω)	R_{ct} (Ω)	C_{dl} (mF)	p
0	0.60	44.27	61.67	0.48	0.947	44.60	46.83	0.76	0.935
0	0.65	44.86	21.19	0.45	0.915	44.44	17.29	0.69	0.914
0.3	0.65	48.22	52.87	0.45	0.962	45.68	31.27	0.68	0.975

3.1.10 Ethanol oxidation on the poly[NPs-Ni(OH)₂SaltMe]-PS_{high} and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalysts

The ethanol oxidation reaction (EOR) on the poly[NPs-Ni(OH)₂SaltMe]-PS_{high} and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalysts follows the EC' mechanism.¹⁰¹ This mechanism involves two stages: (i) electrochemical and (ii) chemical. During the first stage, Ni³⁺OOH-type active sites are electrogenerated according to Equation 3.1-2.



In the second stage, the chemical oxidation of ethanol to acetic acid occurs on the electrogenerated poly(NPs-Ni³⁺OOHSalen) active sites, while the catalyst is simultaneously regenerated, as described in Equation 3.1-3.



The observed increase in current density after the addition of ethanol indicates catalysis. According to Equation 3.1-3, the Ni³⁺ species are consumed during the chemical process, leading to a decrease in the cathodic peak current of the reduction of Ni³⁺ to the Ni²⁺ compared to this peak in the pure 0.2 M NaOH_{aq}.

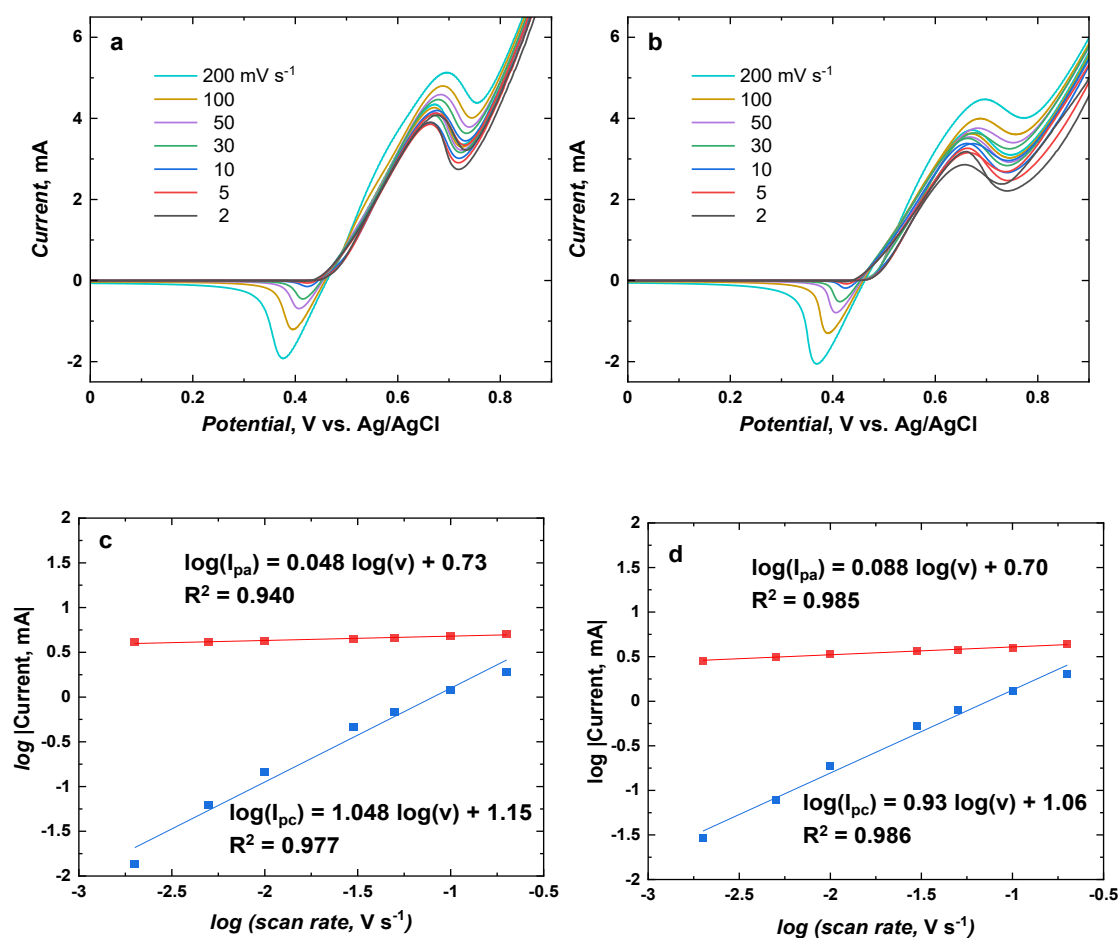


Figure 3.1-15. The CV curves of (a) poly[NPs-Ni(OH)₂SaltMe-PS_{high}] and (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} registered in 0.2 M NaOH_{aq} in the presence of 0.3 M ethanol registered at different scan rates. (c, d) The logarithm of the anodic (red curve) and cathodic (blue curve) peak current dependence on the logarithm of the scan rate.

The high accessibility of Ni³⁺OOH-type active sites is crucial for achieving high catalytic activity. Therefore, in this dissertation, the tuning of the morphology of poly(NiSalen) precursors is described, as it governs the arrangement of Ni(OH)₂ NPs in the poly(Salen) matrix. The scan rate experiment allowed varying the time between the anodic and cathodic processes, i.e., decreasing the scan rate provides more time for the chemical step, resulting in a decrease in the amount of Ni²⁺ species due to the reduction of accessible Ni³⁺ species (Fig. 3-1-15).

The surface concentration (Γ)¹⁷¹ of poly(NPs-Ni³⁺OOHSalen) active sites was determined from the cathodic parts of the CV curves to analyze the ethanol electrooxidation process on the poly[NPs-Ni(OH)₂SaltMe]-PS_{high} and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalysts. These values were determined for all scan rates for the following three cycles in the absence (Fig. 3.1-12 and 3.1-13) and presence (Fig. 3.1-15) of 0.3 M ethanol in 0.2 M NaOH_{aq} according to Equation 3.1-4.

$$\Gamma = \frac{Q_c}{nFA} \quad (3.1-4)$$

Where Q_c is the cathodic charge, n is the number of exchanged electrons, F is a Faraday constant, and A is the geometric area of the electrode. Determined Γ values were presented in Table 3.1-5.

Table 3.1-5. Ni³⁺OOH centers surface concentrations calculated from the multi-scan rate CV experiments within three consecutive cycles performed for poly[NPs-Ni(OH)₂SaltMe]-PS_{high} and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalysts in 0.2 M NaOH_{aq} in the absence and presence of 0.3 M ethanol.

ν mV s ⁻¹	Γ of poly[NPs-Ni(OH) ₂ SaltMe]-PS _{high}			Γ of poly[NPs-Ni(OH) ₂ SaltMe]-PS _{high} with 0.3 M ethanol			Γ of poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe]-PS _{low}			Γ poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe]-PS _{low} with 0.3 M ethanol		
	$\mu\text{mol cm}^{-2}$			$\mu\text{mol cm}^{-2}$			$\mu\text{mol cm}^{-2}$			$\mu\text{mol cm}^{-2}$		
	cycle 1	cycle 2	cycle 3	cycle 1	cycle 2	cycle 3	cycle 1	cycle 2	cycle 3	cycle 1	cycle 2	cycle 3
2	0.093	0.086	0.087	0.012	0.013	0.012	0.094	0.090	0.093	0.019	0.018	0.019
5	0.082	0.083	0.083	0.024	0.024	0.021	0.093	0.088	0.090	0.026	0.024	0.025
10	0.082	0.080	0.082	0.027	0.027	0.028	0.089	0.088	0.088	0.031	0.033	0.032
30	0.081	0.078	0.077	0.037	0.035	0.036	0.081	0.080	0.082	0.041	0.040	0.040
50	0.074	0.075	0.074	0.040	0.039	0.038	0.077	0.077	0.075	0.043	0.043	0.043
100	0.071	0.071	0.073	0.044	0.043	0.043	0.074	0.075	0.076	0.045	0.046	0.045
200	0.066	0.066	0.065	0.045	0.045	0.045	0.069	0.069	0.070	0.048	0.048	0.048

The determined Γ values were lower in the presence of 0.3 M ethanol due to the reduction of accessible Ni³⁺-type active sites to the Ni²⁺ species during the backward scan, according to the EC' mechanism. Similar Γ values for the three following cycles indicated that catalyst active sites were regenerated during the CV cycling (Table 3.1-5). Higher Γ values obtained for

poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalyst can explain better catalytic efficiency of this catalyst (Table 3.1-2).

Electrochemically active surface area (A_{ECSA}) of poly[NPs-Ni(OH)₂SaltMe]-PS_{high} and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalysts was estimated with the oxalate method¹⁵¹ according to Equation 2.3-17 and from Figure 3.1-16. Estimated A_{ECSA} was 17.5 cm² and 33.0 cm² for poly[NPs-Ni(OH)₂SaltMe]-PS_{high} and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low}, respectively, which is in agreement with surface concentration values where a higher amount of active centers was obtained for poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalyst.

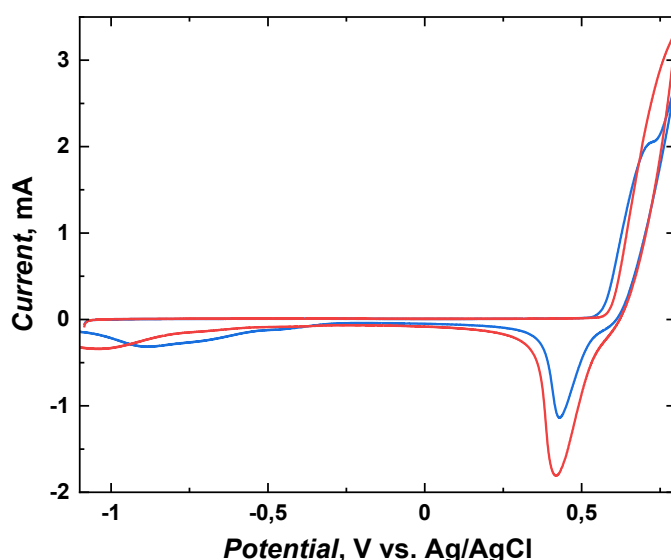


Figure 3.1-16. CV electrochemical response of poly[NPs-Ni(OH)₂SaltMe]-PS_{high} (blue) and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} (red) at 150 mV s⁻¹ in 0.1 M NaOH_{aq} containing 0.08 M C₂O₄²⁻.

The EIS measurements were conducted in the presence of 0.3 M ethanol at a potential of 0.65 V vs. Ag/AgCl (Figure 3.1-17). The R_{ct} values obtained after fitting to the experimental data were higher than R_{ct} measured in pure 0.2 M NaOH_{aq} (Table 3.1-4), indicating that the charge transfer was slower during the ethanol electrooxidation. Furthermore, the lower R_{ct} values obtained for poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalyst (Table 3.1-4) indicated that the electrocatalytic

process was comparably faster on this catalyst. The R_Ω value (Table 3.1-4) in the presence of ethanol was higher for poly[NPs-Ni(OH)₂SaltMe]-PS_{high}, suggesting that the ethanol adsorbed more strongly on this catalyst. The data described indicated that the poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalyst exhibited better catalytic performance for ethanol electrooxidation.

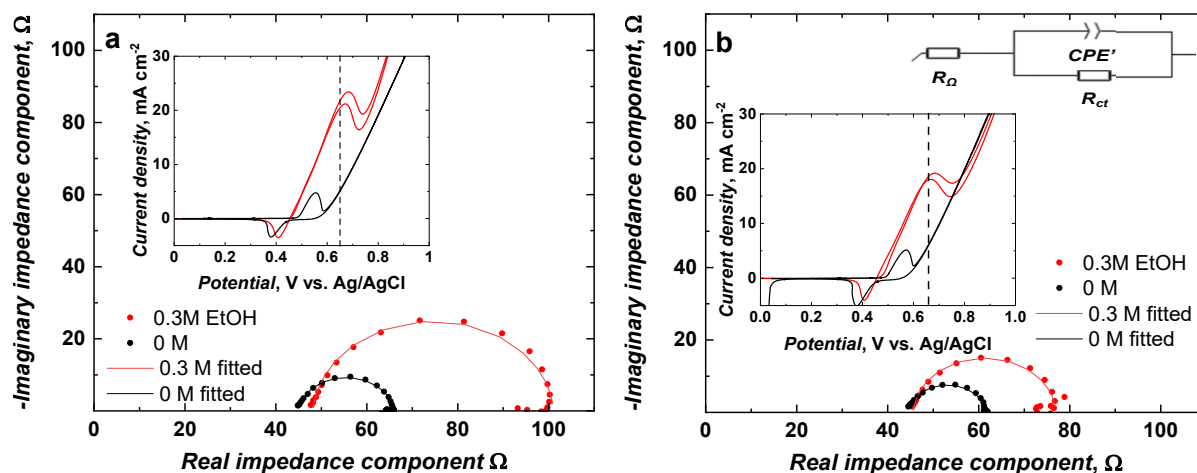


Figure 3.1-17. Nyquist plots for (a) poly[NPs-Ni(OH)₂SaltMe]-PS_{high}, and (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} prepared based on EIS measurements registered in 0.2 M NaOH_{aq} in the absence and presence of 0.3 M ethanol, at the potential of 0.65 V. Insets display CV curve of poly[NPs-Ni(OH)₂SaltMe]-PS_{high}, and (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} registered at 50 mV s⁻¹ in 0.2 M NaOH_{aq} in absence and presence of 0.3 M ethanol. Inset: a modified Randles-Ershler equivalent electric circuit composed of R_Ω , CPE' , and R_{ct} electrical elements used for fitting the individual electrical circuit elements' values to the experimental data.

The quantum chemical calculations on the DFT level (Fig. 3.1-18, Tables 3.1-6, and 3.1-7) were utilized to optimize the structures of a single catalytic center of Ni(OH)₂ embedded in poly(SaltMe) and poly(*meso*-SaldMe) matrices to comprehend the enhanced catalytic performance of the poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalyst. The negative values of the sum of electronic and thermal free energies obtained for optimized catalytic centers structures

of NP-Ni(OH)₂SaltMe and NP-Ni(OH)₂SaldMe indicated their high stability (Tables 3.1-6 and 3.1-7). The Ni(OH)₂ center is positioned in front of the space-folded plane of the *meso*-SaldMe matrix (Fig. 3.1-18a). While the Ni center of Ni(OH)₂ embedded in SaltMe (Fig. 3.1-18b) is placed in the matrix plane and stabilized in this position by hydrogen bonding to imine nitrogen. This optimization revealed that the axial access of ethanol to the Ni(OH)₂ centers was facilitated in *meso*-NP-Ni(OH)₂SaldMe, thus explaining the better catalytic performance of the poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalyst.

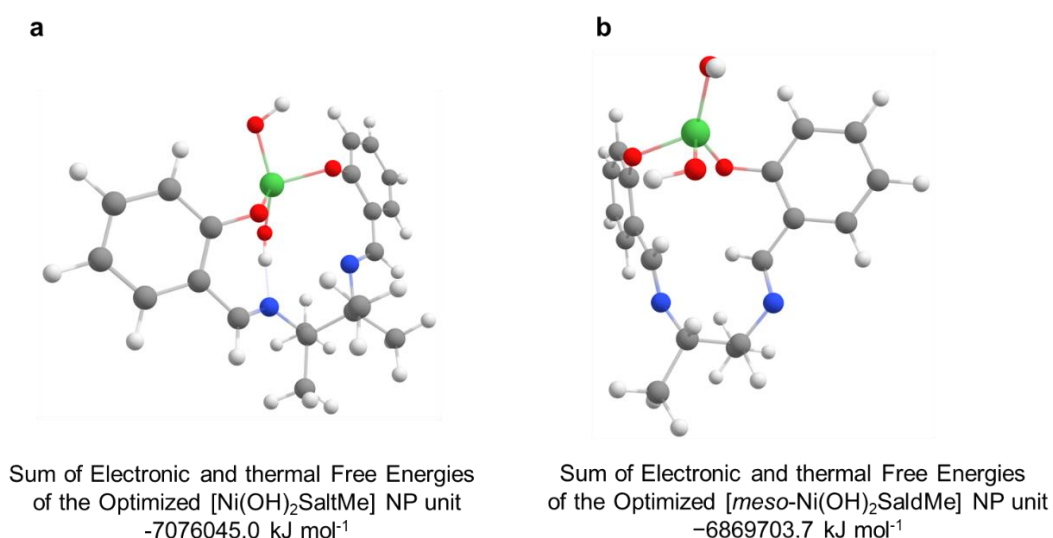


Figure 3.1-18. The DFT level optimized molecular structures of single catalytic centers Ni(OH)₂ embedded in (a) SaltMe and (b) *meso*-SaldMe matrix with the use of Tao-Perdew Staroverov-Scuseria (TPSS) functional.

Table 3.1-6. Calculated binding energies of *meso*-NP-Ni(OH)₂SaldMe.

Complex	Calculated quantity	Energy of complex [kJ/mol]	Sum of energies of components [kJ/mol]	Complex binding energies [kJ/mol]
<i>meso</i> -NP-Ni(OH) ₂ SaldMe	Sum of Electronic and Zero-Point Energies	-6869559.9	-6869457.9	-102.0
<i>meso</i> -NP-Ni(OH) ₂ SaldMe	Sum of Electronic and thermal Free Energies	-6869703.7	-6869671.6	-32.1

Table 3.1-7. The calculated binding energies of NP-Ni(OH)₂SaltMe.

Complex	Calculated quantity	Energy of complex [kJ/mol]	Sum of Energies of components [kJ/mol]	Complex binding energies [kJ/mol]
NP-Ni(OH) ₂ SaltMe	Sum of Electronic and Zero-Point Energies	-7075890.0	-7075820.5	-69.5
NP-Ni(OH) ₂ SaltMe	Sum of Electronic and thermal Free Energies	-7076045.0	-7076040.0	-5.0

3.1.11 Effect of the reinforcing properties of reduced graphene oxide on the electrocatalytic performance of poly[NPs-Ni(OH)₂SaltMe]-PS_{high} and poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} catalysts

The properties of poly(NiSalen)s, such as the conjugated electronic structure, intrinsic conductivity, higher surface area, and mechanical strength, can be enhanced by incorporating RGO as a reinforcing material.⁵⁴

The poly(NiSalen) and poly(*meso*-NiSaldMe) were electrodeposited on a RGO-coated CP electrode⁵⁴ from 1 mM monomer solution in 0.1 M TBAPF₆/ACN. The deposition of RGO-poly(NiSaltMe) and RGO-poly(*meso*-NiSaldMe) was conducted under multi-scan PD

conditions, utilizing a high (100 mV s^{-1}) scan rate within the extended potential window of 0.0-1.4 V for 16 cycles.

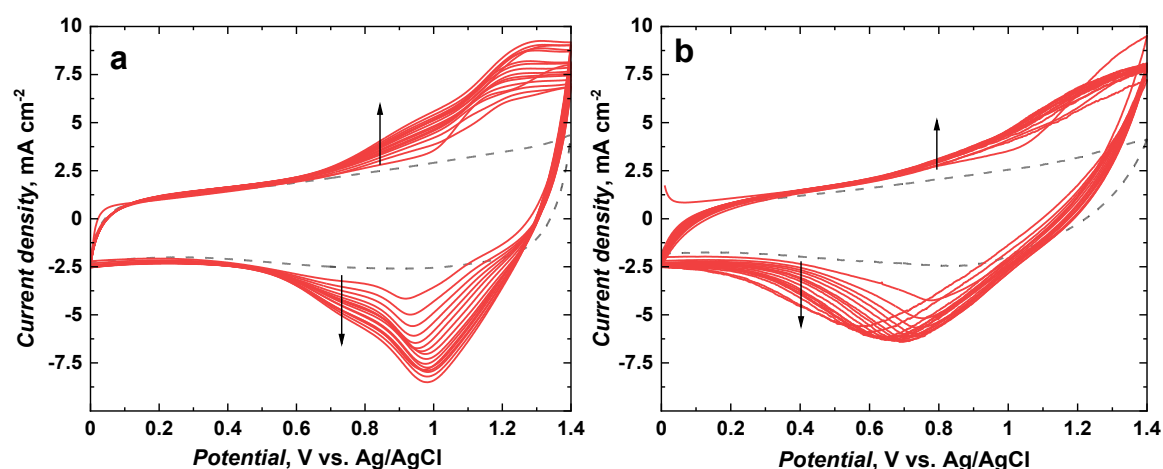


Figure 3.1-19. Multi-cyclic PD curves (red) of oxidative electropolymerization of 1 mM (a) NiSaltMe, and (b) *meso*-NiSaldMe at 100 mV s^{-1} in an ACN solution of 0.1 M (TBA)PF₆. The black dash curve represents CV performed on the RGO-coated CP electrode in the absence of monomer.

The currents observed during polymerization of NiSaltMe and *meso*-NiSaldMe on RGO-coated CP electrodes (Fig. 3.1-19) were notably higher compared to those observed on bare CP electrodes (Fig. 3.1-1b and d). The charges passed during electropolymerizations were 578 and 621 mC cm^{-2} for RGO-poly(NiSaltMe) and RGO-poly(*meso*-NiSaldMe), respectively.

These precursor composite polymers exhibited enhanced stability during the NP generation step. The stabilization of the oxidation ($\text{Ni}^{2+}/\text{Ni}^{3+}$) and reduction ($\text{Ni}^{3+}/\text{Ni}^{2+}$) peaks required at least 150-300 cycles in 0.2 M NaOH_{aq}. Moreover, the potential range during the potential-driven transformation of RGO-poly(NiSalen)s into RGO-poly[NPs-Ni(OH)₂SaltMe] and RGO-poly[*meso*-NPs-Ni(OH)₂SaldMe] was enlarged to 1.5 V.

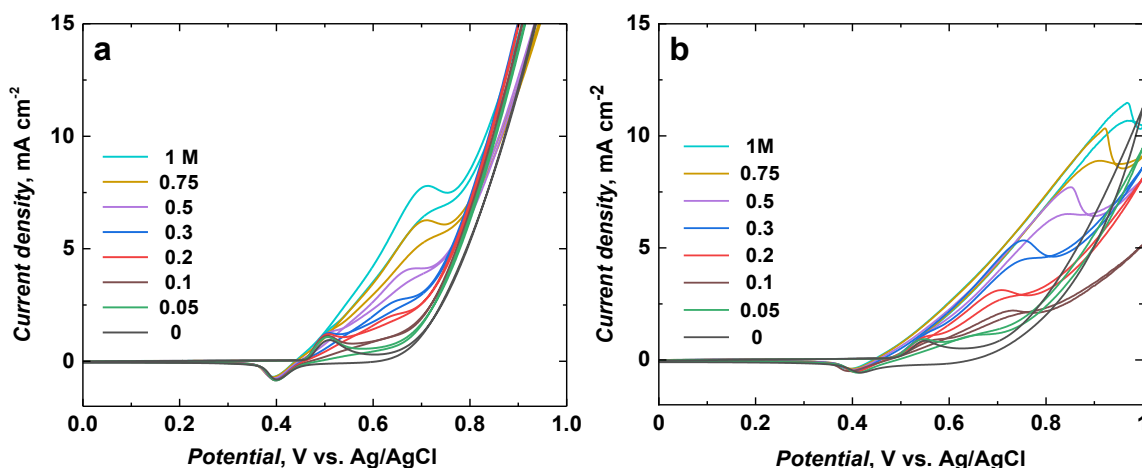


Figure 3.1-20. The catalytic CV responses of (a) RGO-poly[NPs-Ni(OH)₂SaltMe] and (b) RGO-poly[*meso*-NPs-Ni(OH)₂SaldMe] in the presence of various ethanol concentrations performed at 50 mV s⁻¹ in 0.2 M NaOH_{aq}.

The electrocatalytic properties of the RGO-poly[NPs-Ni(OH)₂SaltMe] and RGO-poly[*meso*-NPs-Ni(OH)₂SaldMe] catalysts were evaluated in the presence of various concentrations of ethanol (Fig. 3.1-20). It was observed that RGO-poly[NPs-Ni(OH)₂SaltMe] (Fig. 3.1-20a) exhibited lower electrocatalytic performance. The catalytic currents obtained for RGO-poly[NPs-Ni(OH)₂Salen] catalysts were lower than those for poly[NPs-Ni(OH)₂Salen] catalysts, likely because only a part of the poly(NiSalen)s was transformed into Ni(OH)₂ in such a composite. Thus, the lower catalytic current can be associated with the lower population of Ni(OH)₂-based active species. It indicates that the enhancement of the electrochemical stability of the poly(NiSalen)s by the reinforcement with RGO did not improve the electrocatalytic properties of the catalysts generated from these samples.

3.2 Electrocatalytic properties of the Ni(OH)₂-type NPs derived from substituted poly(NiSalen-3dOMe) precursors

The synthesis of NiSaltMe-3dOMe and *meso*-NiSaldMe-3dOMe precursor complexes, with a methoxy (-OCH₃) substituent in both 3-positions of the salicylaldehyde moiety, was encouraged by the electrocatalysis results obtained for Ni(OH)₂-type NPs derived from phenyl ring unsubstituted poly(NiSaltMe) and poly(*meso*-NiSaldMe) described in Chapter 3.1. Towards that, first NiSaltMe-3dOMe and *meso*-NiSaldMe-3dOMe complexes were synthesized and characterized by NMR. Next, precursors poly(NiSaltMe-3dOMe) and poly(*meso*-NiSaldMe-3dOMe) were deposited under PD and PS conditions, followed by their transformation into poly[NPs-Ni(OH)₂SaltMe-3dOMe] and poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe] catalysts.

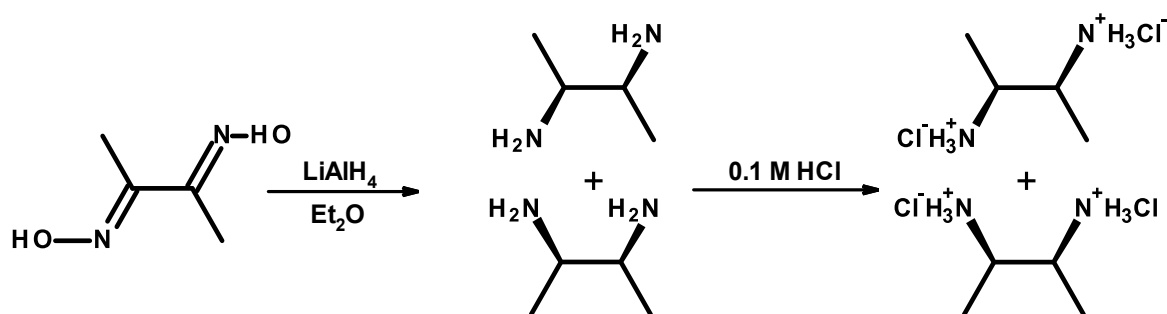
This chapter describes how introducing ED methoxy (-OCH₃) substituents onto the phenyl rings of poly(NiSalen)s differing in the configuration of the methyl (-CH₃) substituted imine bridge affects their potential-driven transformation process and the catalytic properties of Ni(OH)₂-type NPs. This idea grew from earlier studies of *meso*-NiSaldMe-3dMe and poly(*meso*-NiSaldMe-3dMe) containing methyl substituents (-CH₃) in both 3-positions of the salicylaldehyde moiety.^{18,134} The increased electron density of poly(*meso*-NiSaldMe-3dMe) extended the electroactivity range, thereby shifting the onset potentials of electrooxidation and electroreduction toward more negative potentials relative to its phenyl-ring-unsubstituted poly(*meso*-NiSaldMe) analog.¹³⁴ Moreover, the potential-driven transformation of poly(*meso*-NiSaldMe-3dMe) in alkaline media into Ni(OH)₂-type NPs embedded in poly(*meso*-SaldMe-3dMe) matrix was studied on the indium tin oxide (ITO) electrode.¹⁷² With this in mind, as mentioned above, NiSaltMe-3dOMe and *meso*-NiSaldMe-3dOMe complexes with a more ED substituent (-OCH₃) were synthesized. To establish a correlation between the morphology of

the poly(NiSalen-3dOMe) precursors, the poly[NPs-Ni(OH)₂Salen-3dOMe] catalysts, and their catalytic activity, both precursors and catalysts were imaged with the SEM and TEM.

3.2.1 Synthesis of the NiSaltMe-3dOMe and *meso*-NiSaldMe-3dOMe complexes

The *meso*-2,3-diaminobutane dihydrochloride was synthesized according to the procedure.^{15,130,135}

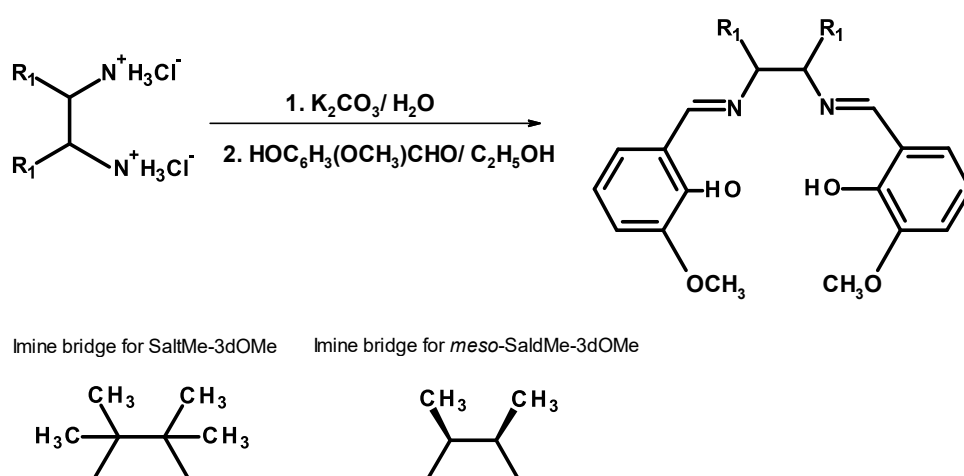
To a cooled (0 °C) anhydrous diethyl ether solution (250 ml) of the dimethylglyoxime (3 g), the same amount of lithium aluminum hydride was added. This mixture was stirred for 72 hours under an argon atmosphere. Next, the reaction was cooled to -78 °C and quenched first with water, then with 15% NaOH, and finally with water. The mixture was warmed to room temperature and stirred for 4 h. Subsequently, the mixture was dried with K₂CO₃, filtered through a pad of Celite, and the solvent was removed under decreased pressure. The residue was neutralized with 1 M HCl until the pH was close to 7, as indicated by universal indicator. Next, with the azeotropic distillation with toluene, the solution was evaporated to dryness. After that, two products were obtained: *meso*-2,3-diaminobutane dihydrochloride and *D, L*-diaminobutane dihydrochloride (Scheme 3.2-1), which were separated by fractional crystallization from methanol. After separation, 0.725 g of *meso*-2,3-diaminobutane dihydrochloride was obtained.



Scheme 3.2-1. Synthesis steps of *meso*-2,3-diaminobutane dihydrochloride and D, L-diaminobutane dihydrochloride.

In the second step, 2,3-dimethyl-*N, N'*-bis(3-methoxysalicylidene)-2,3-diaminobutane and *meso-N, N'*-bis(3-methoxysalicylidene)-2,3-diaminobutane ligands were synthesized following the steps (adapted based on procedures developed earlier)^{15,130,135} presented in Scheme 3.2-2.

The aqueous solution of 1 equivalent (eq) of 2,3-dimethyl-2,3-diaminobutane dihydrochloride or *meso*-2,3-diaminobutane dihydrochloride was stirred with 2.2 eq of K₂CO₃ under an argon atmosphere for 40 min. Subsequently, ethanol was added to the solution, and the mixture was heated to 60°C. Next, 2 eq of O-vanillin were added to this solution, and the reaction was carried out for 6 h under reflux conditions. After that mixture was cooled to room temperature, the solvent was removed under reduced pressure. The resulting precipitate was dissolved in chloroform, washed with water, and dried with MgSO₄. Subsequently, chloroform was removed under reduced pressure, and the products were recrystallized from a mixture of dichloromethane and hexane. The quantities and yields of the obtained ligands are presented in Table 3.2-1.



Scheme 3.2-2. Synthesis steps of the SaltMe-3dOMe and *meso*-SaldMe-3dOMe ligands.

The structures of SaltMe-3dOMe and *meso*-SaldMe-3dOMe ligands were confirmed by NMR spectroscopy (Fig. A1-1 – Fig. A1-4).

SaltMe-3dOMe: ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 1.42 (s, 12H, CH_3C); 3.90 (s, 6H, CH_3O); 6.76 (t, 2H, arom-4); 6.86 (dd, 2H, arom-3); 6.89 (dd, 2H, arom-5); 8.33 (s, 2H, $\text{N}=\text{CH}$); 14.79 (s, 2H, OH).

^{13}C NMR (CDCl_3 , 400 MHz, ppm): δ 22.97 ($\text{C1H}_3\text{C}$); 55.95 ($\text{C9H}_3\text{O}$); 65.04 ($\text{CH}_3\text{C2}$); 113.63 (arom-C7); 117.41 (arom-C5); 118.20 (arom-C4); 123.22 (arom-C6); 148.65 (C10-OH); 153.17 (arom-C8); 161.76 ($\text{N}=\text{C3H}$).

All signals from 28 protons and 10 carbons were visible in the ^1H NMR and ^{13}C NMR spectra, respectively.

***meso*-SaldMe-3dOMe** ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 1.30 (d, 6 H, CH_3CH); 3.51 (q, 2 H, CH_3CH); 3.90 (s, 6 H, CH_3O); 6.82 (t, 2 H, arom-4); 6.90 (dd, 2 H, arom-3); 6.93 (dd, 2 H, arom-5); 8.39 (s, 2 H, $\text{N}=\text{CH}$); 13.77 (s, 2 H, OH).

^{13}C NMR (CDCl_3 , 400 MHz, ppm): δ 19.23 ($\text{C1H}_3\text{C}$); 55.08 ($\text{C9H}_3\text{O}$); 69.13 (s, $\text{CH}_3\text{C2}$); 114.05 (arom-C7); 118.05 (arom-C5); 118.52 (arom-C4); 123.06 (arom-C6); 148.38 (C10-OH); 151.54 (arom-C8); 161.33 ($\text{N}=\text{C3H}$).

All signals from 24 protons and 10 carbons were visible in the ^1H NMR and ^{13}C NMR spectra, respectively.

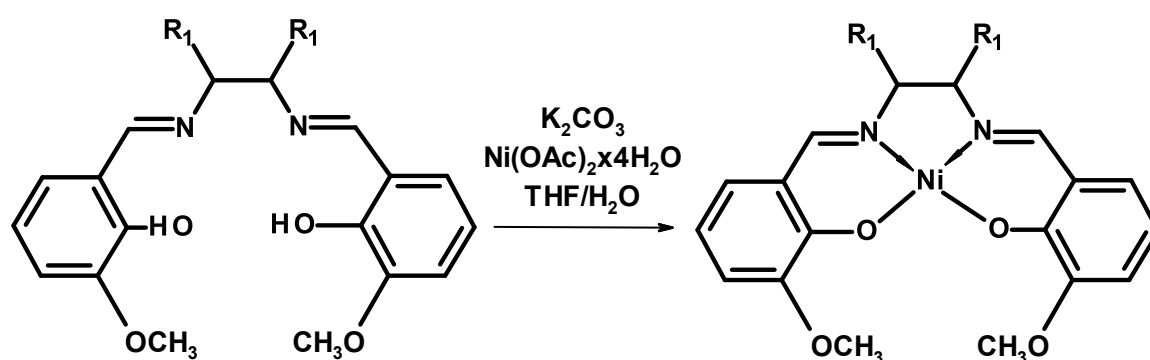
Table 3.2-1. Summarization of the amount of substrates used and yield of products in the syntheses of different Salen ligands and NiSalen complexes.

Substrates	m g	n mol	eq	M g/mol	Product	m g	yield %	M g/mol
2,3-dimethyl-2,3-diaminobutane dihydrochloride	0.500	2.264	1	189.1	SaltMe-3dOMe	0.870	98.5	384.5

K ₂ CO ₃	0.688	4.980	2.2	138.2				
O-vanillin	0.688	4.528	2	152.2				
<i>meso</i> -2,3-diaminobutane dihydrochloride	0.070	0.435	1	161.1				
K ₂ CO ₃	0.132	0.957	2.2	138.2	<i>meso</i> -SaldMe-3dOMe	0.114	73.5	356.4
O-vanillin	0.132	0.870	2	152.2				
SaltMe-3dOMe	0.181	0.471	1	384.5				
Ni(COOCH ₃) ₂ × 4 H ₂ O	0.117	0.471	1	248.8	NiSaltMe-3dOMe	0.185	89	441.1
K ₂ CO ₃	0.130	0.941	2	138.2				
<i>meso</i> -SaldMe-3dOMe	0.114	0.320	1	356.4				
Ni(COOCH ₃) ₂ × 4 H ₂ O	0.080	0.320	1	248.8	<i>meso</i> -NiSaldMe-3dOMe	0.117	89	413.1
K ₂ CO ₃	0.088	0.640	2	138.2				

In the last step, 2,3-dimethyl-*N, N'*-bis(3-methoxysalicylidene)-2,3-butanediaminonickel and *meso-N, N'*-bis(3-methoxysalicylidene)-2,3-butanediaminonickel were synthesized according to the procedure presented in Scheme 3.2-3.

1 eq of Nickel (II) acetate tetrahydrate, 2 eq of K₂CO₃, and 1 eq of the respective ligand, synthesized in the 1st step, were added to the water and THF (1:1, v/v). This mixture was stirred for 6 h at 60°C under an argon atmosphere. The residual product was filtered, washed with water, and crystallized from anhydrous acetonitrile. The yields of the obtained complexes are presented in Table 3.2-1.



Scheme 3.2-3. Synthesis step of the NiSaltMe-3dOMe and *meso*-NiSaldMe-3dOMe complexes.

The structures of NiSaltMe-3dOMe and *meso*-NiSaldMe-3dOMe were confirmed by NMR spectroscopy (Fig. A1-5 – Fig. A1-8).

NiSaltMe-3dOMe: ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 1.44 (s, 12 H, CH_3C); 3.80 (s, 6 H, CH_3O); 6.47 (t, 2 H, arom-4); 6.68 (dd, 2 H, arom-3); 6.75 (dd, 2 H, arom-5); 7.49 (s, 2 H, $\text{N}=\text{CH}$).

^{13}C NMR (CDCl_3 , 400 MHz, ppm): δ 24.70 ($\text{C}_1\text{H}_3\text{C}$); 55.37 ($\text{C}_9\text{H}_3\text{O}$); 71.67 (CH_3C_2); 112.66 (C7); 113.90 (arom-C5); 119.71 (arom-C4); 123.50 (arom-C6); 151.16 (arom-C10); 156.08 (arom-C8); 157.99 ($\text{N}=\text{C}_3\text{H}$).

On the NiSaltMe-3dOMe ^1H NMR and ^{13}C NMR spectra were visible signals from all 26 protons and 10 carbons, respectively.

***meso*-NiSaldMe-3dOMe:** ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 1.32 (d, 6 H, CH_3CH); 3.53 (q, 2 H, CH_3CH); 3.80 (s, 6 H, CH_3O); 6.46 (t, 2 H, arom-4); 6.68 (dd, 2 H, arom-3); 6.71 (d, 2 H, arom-5); 7.38 (s, 2 H, $\text{N}=\text{CH}$).

^{13}C NMR (CDCl_3 , 400 MHz, ppm): δ 15.04 ($\text{C}_1\text{H}_3\text{C}$); 55.29 ($\text{C}_9\text{H}_3\text{O}$); 66.55 (s, CH_3C_2); 112.46 (arom-C7); 113.96 (arom-C4); 119.51 (arom-C5); 123.24 (arom-C6); 151.20 (C10-OH); 159.64 ($\text{N}=\text{C}_3\text{H}$).

All 22 protons were visible for the *meso*-NiSaldMe-3dOMe in the ^1H NMR spectrum. One quaternary carbon atom was invisible in the ^{13}C NMR spectrum because of its long relaxation time.

3.2.2 Poly(NiSaltMe-3dOMe) and poly(*meso*-NiSaldMe-3dOMe) precursors electrodeposition and electrochemical characterization

Poly(NiSalen-3dOMe) precursor polymers were deposited on the CP electrode surface under the PD (Fig. 3.2-1) and PS (Fig. 3.2-2) conditions with an amount of charge similar to 137 mC cm^{-2} . This charge was selected for depositing precursors because the unsubstituted poly[*meso*-Ni(OH)₂SaldMe] catalysts generated from the poly(*meso*-NiSaldMe), deposited with this charge, provided the highest catalytic activity toward ethanol electrooxidation (Chapter 3.1).

Poly(NiSalen-3dOMe)-PD precursors were deposited on the CP electrode by oxidative electropolymerization under PD conditions with a scan rate of 100 mV s^{-1} in the potential range of 0.0-1.2 V vs. Ag/Ag⁺ (Fig. 3.2-1). To deposit polymer with a charge close to 137 mC cm^{-2} , 21 (Fig. 3.2-1a) and 22 (Fig. 3.2-1b) polymerization cycles were needed for poly(NiSaltMe-3dOMe)-PD and poly(*meso*-NiSaldMe-3dOMe)-PD, respectively. The current increase in the subsequent polymerization CV cycles indicated successful deposition of conducting poly(NiSaltMe-3dOMe)-PD and poly(*meso*-NiSaldMe-3dOMe)-PD layers.¹⁵

In the first electropolymerization cycle of 1 mM NiSaltMe-3dOMe (Fig. 3.2-1a) and *meso*-NiSaldMe-3dOMe (Fig. 3.2-1b), two anodic peaks were observed. For both polymers, the first peak was at $\sim 0.9 \text{ V}$, and can be assigned to the oxidation of both NiSaltMe-3dOMe and *meso*-NiSaldMe-3dOMe monomers to bisphenolic cation radicals. The second oxidation peak was at $\sim 1.03 \text{ V}$ (Fig. 3.2-1a) and $\sim 0.98 \text{ V}$ (Fig. 3.2-1b), corresponding to the oxidation of the bisphenolic cation radical to bisphenolic cations. The oxidation peaks of the NiSalen-3dOMe monomers were shifted towards lower potentials by more than 100 mV compared to the unsubstituted NiSalen monomers (Chapter 3.1, Fig 3.1.1). The electrooxidation onset belonging to monomers oxidation to cation radical form indicates that oxidation of the

substituted NiSalen-3dOMe monomer is easier than that of the unsubstituted NiSalen (Chapter 3.1, Fig 3.1.1) complex.

During subsequent electropolymerization cycles, three anodic waves centered at ~ 0.57 , ~ 0.9 , and ~ 1.1 V for poly(NiSaltMe-3dOMe)-PD (Fig. 3.2-1a) and ~ 0.45 , ~ 0.8 , and ~ 1.0 V for poly(*meso*-NiSaldMe-3dOMe)-PD (Fig. 3.2-1b) were observed. These peaks corresponded to the initial electrochemical doping and the generation of bisphenolic radical cations within the already deposited polymer layers. For the poly(*meso*-NiSaldMe-3dOMe)-PD, the anodic peaks were much broader than for poly(NiSaltMe-3dOMe)-PD, indicating faster charge transport in poly(*meso*-NiSaldMe-3dOMe)-PD. The highest current observed for poly(*meso*-NiSaldMe-3dOMe)-PS indicated that this polymer contains the highest number of electroactive species involved in charge transport. Moreover, comparison of the polymerization curves of phenyl-ring substituted poly(NiSaltMe-3dOMe) and poly(*meso*-NiSaldMe-3dOMe) (Fig. 3.2-1) with those of unsubstituted poly(NiSaltMe), and poly(*meso*-NiSaldMe) (Chapter 3.1, Fig. 3.1-1) reveals clear differences in peak shape, indicating that the electronic structure is sensitive to modifications in phenyl ring environment.^{134,173,174}

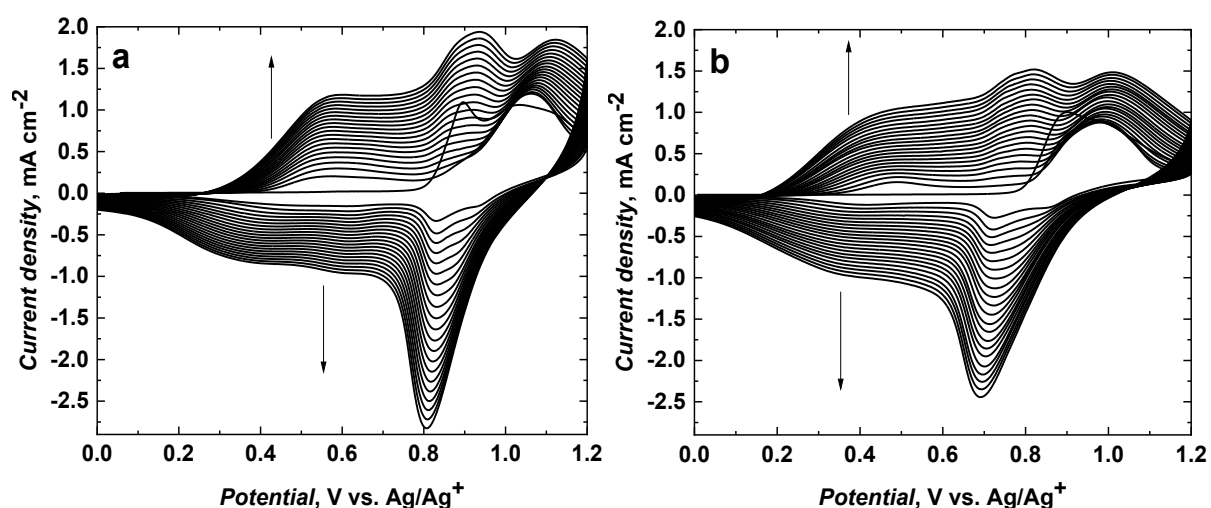


Figure 3.2-1. Multi-cyclic PD curve of oxidative electropolymerization of 1 mM (a) NiSaltMe-3dOMe, and (b) *meso*-NiSaldMe-3dOMe on CP electrode in an ACN solution of 0.1 M (TBA)PF₆ registered at 100 mV s⁻¹.

Poly(NiSaltMe-3dOMe)-PS and poly(*meso*-NiSaldMe-3dOMe)-PS precursors were deposited under PS conditions by keeping a constant potential of 1.3 V vs. Ag/Ag⁺ for 1300 s (Fig. 3.2-2a) and 1463 s (Fig. 3.2-2b), respectively, to obtain the amount of charge close to 137 mC cm⁻². For PS deposition, 1.3 V was applied to ensure that the oxidation potential for two-electron transfer was reached, which was required for depositing a conductive polymer with desirable properties.

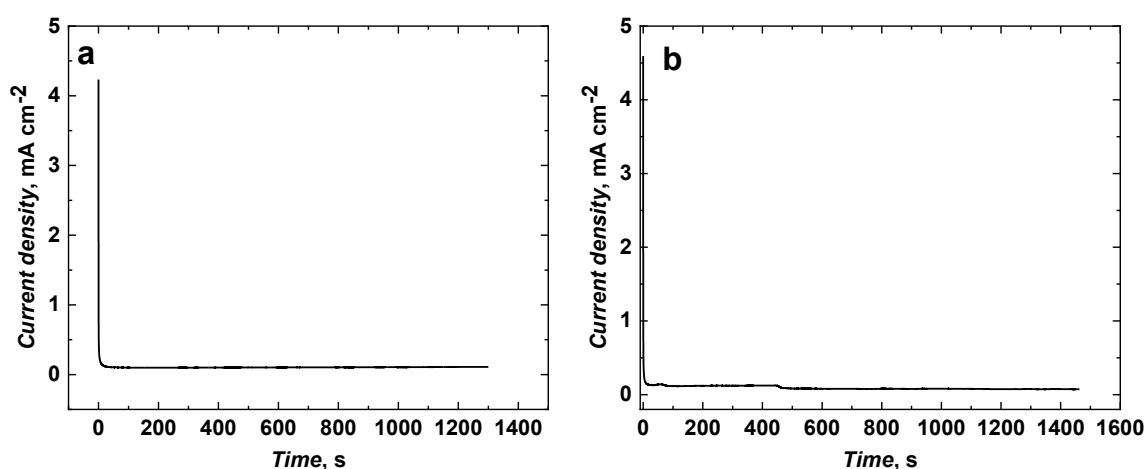


Figure 3.2-2. PS deposition of 1 mM of (a) NiSaltMe-3dOMe and (b) *meso*-NiSaldMe-3dOMe on the CP electrode in an ACN solution of 0.1 M (TBA)PF₆ at a potential of 1.3 V vs. Ag/Ag⁺. Amount of charge during deposition was 137.1 mC cm⁻².

Next, the poly(NiSalen-3dOMe)s were rinsed with a solvent and transferred to a monomer-free 0.1 M (TBA)PF₆/ACN solution, and the electrochemical responses of these poly(NiSalen-3dOMe)s were registered. These CV responses provided a deeper understanding of the redox processes occurring in the precursor polymers (Fig. 3.2-3). CV curves recorded at 20 mV s⁻¹ scan rate exhibited two anodic peaks, suggesting the occurrence of two faradaic processes involved in the polymer charge transport. The first peak was centered at ~0.50 V for poly(NiSaltMe-3dOMe)-PS and at ~0.45 V for poly(*meso*-NiSaldMe-3dOMe)-PS. This peak

appeared at lower potentials for PD deposited precursors. For poly(NiSaltMe-3dOMe)-PD, the peak was at ~ 0.40 V, and for poly(*meso*-NiSaldMe-3dOMe)-PD at ~ 0.30 V. This peak can be assigned to the first electron withdrawal from the polymer, accompanied by the formation of bisphenolic radical cations and charge compensation *via* electrochemical counter-ion doping. The second peak was centered at ~ 0.66 and ~ 0.65 V for poly(NiSaltMe-3dOMe)-PS, and poly(*meso*-NiSaldMe-3dOMe)-PS, respectively and at ~ 0.72 , and ~ 0.67 V for poly(NiSaltMe-3dOMe)-PD, and poly(*meso*-NiSaldMe-3dOMe)-PD, respectively. This peak can be assigned to the withdrawal of the subsequent electron from the polymer, leading to the formation of bisphenolic dications. Moreover, during the electrochemical response in moderately ED media such as ACN, no $\text{Ni}^{2+}/\text{Ni}^{3+}$ oxidation/reduction peaks were observed, as observed in NaOH_{aq} in Chapter 3.1 (Fig. 3.1-5 and 3.1-6).

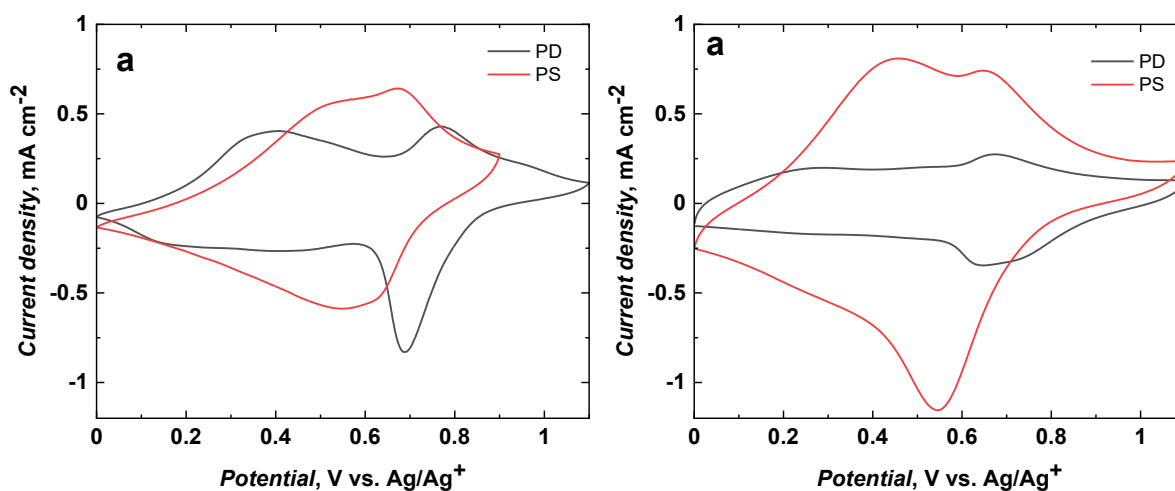


Figure 3.2-3. CV curves for (a) poly(NiSaltMe-3dOMe)-PD (black) and poly(NiSaltMe-3dOMe)-PS (red) (b) poly(*meso*-NiSaldMe-3dOMe)-PD (black) and poly(*meso*-NiSaldMe-3dOMe)-PS (red) film-coated CP electrode in monomer-free ACN solution of 0.1 M (TBA)PF₆, registered at 20 mV s⁻¹.

3.2.3 Morphological characterization of the substituted poly(NiSalen-3dOMe) precursors

SEM imaging (Fig. 3.2-4) revealed that poly(NiSaltMe-3dOMe) and poly(*meso*-NiSaldMe-3dOMe) precursors covered the CP electrode fibers entirely. A closer look indicated that poly(NiSaltMe-3dOMe)s (Fig. 3.2-4a, a', b, b') showed a uniform pattern with occasional bubble-shaped aggregates. Bigger polymer globules were seen in PS-deposited poly(NiSaltMe-3dOMe)-PS. Comparison of phenyl-ring substituted poly(NiSaltMe-3dOMe)s with unsubstituted poly(NiSaltMe) analogs (Chapter 3.1, Fig. 3.1-3) revealed that the poly(NiSaltMe-3dOMe)-PS and poly(NiSaltMe-3dOMe)-PD precursors exhibited rougher and less uniform morphology. Poly(*meso*-NiSaldMe-3dOMe)s (Fig. 3.2-4c, c', d, d') were always composed of larger globular structures, with a rougher surface for poly(*meso*-NiSaldMe-3dOMe)-PD precursor. Another noticeable difference was the population of those globules.

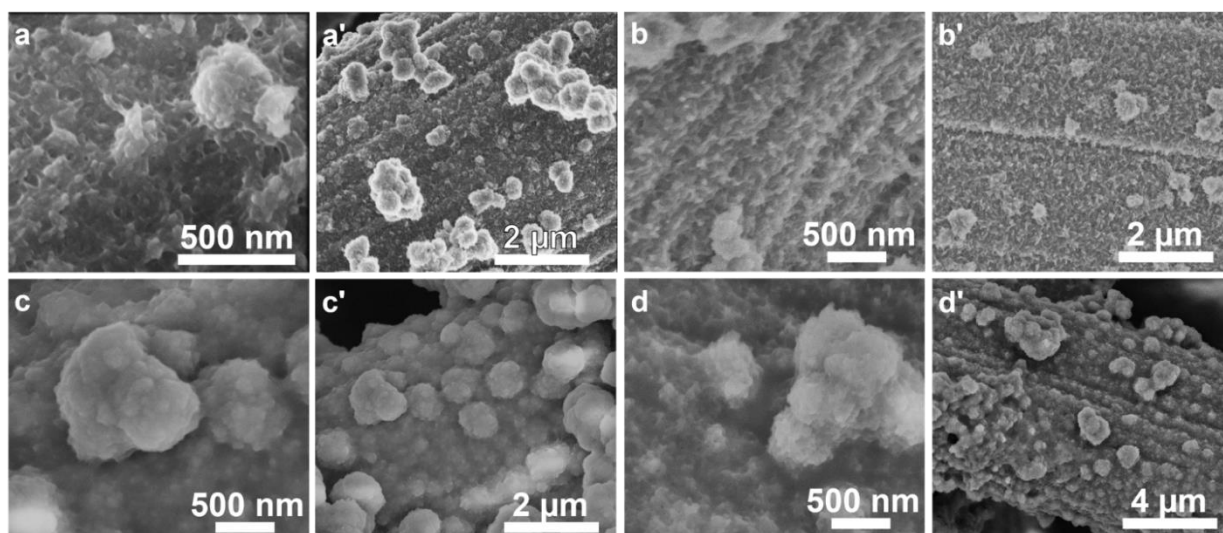


Figure 3.2-4. SEM images of different precursors at two scales: (a, a') poly(NiSaltMe-3dOMe)-PS, (b, b') poly(NiSaltMe-3dOMe)-PD, (c, c') poly(*meso*-NiSaldMe-3dOMe)-PS, and (d, d') poly(*meso*-NiSaldMe-3dOMe)-PD.

TEM imaging (Fig. 3.2-5) followed the observations from SEM. Poly(NiSaltMe-3dOMe)s (Fig. 3.2-5a and b) revealed a uniform pattern, with a more irregular structure observed for the poly(NiSaltMe)-PD precursor (Fig. 3.2-5b). The poly(NiSaltMe-3dOMe)-PD showed irregular grains in the layer, but with a low Ni content (Figure 3.2-5b). The poly(NiSaltMe-3dOMe)-PS (Fig. 3.2-5a) was the most homogeneous, with Ni uniformly distributed over the entire polymer layer. The poly(*meso*-NiSaldMe-3dOMe) layers (Fig. 3.2-5c and d) were composed of irregular globular structures. The most pronounced edge irregularities were observed for the poly(*meso*-NiSaldMe-3dOMe)-PD (Fig. 3.2-5d). The EDX mapping (Fig. 3.2-5a'', b'', c'', d'') confirmed the presence of the Ni and C elements in all polymer samples. The EDX profiling of poly(*meso*-NiSaldMe-3dOMe)-PD (Fig. 3.2-5d'') showed heterogeneous distributions of polymer grains containing Ni in comparison to others.

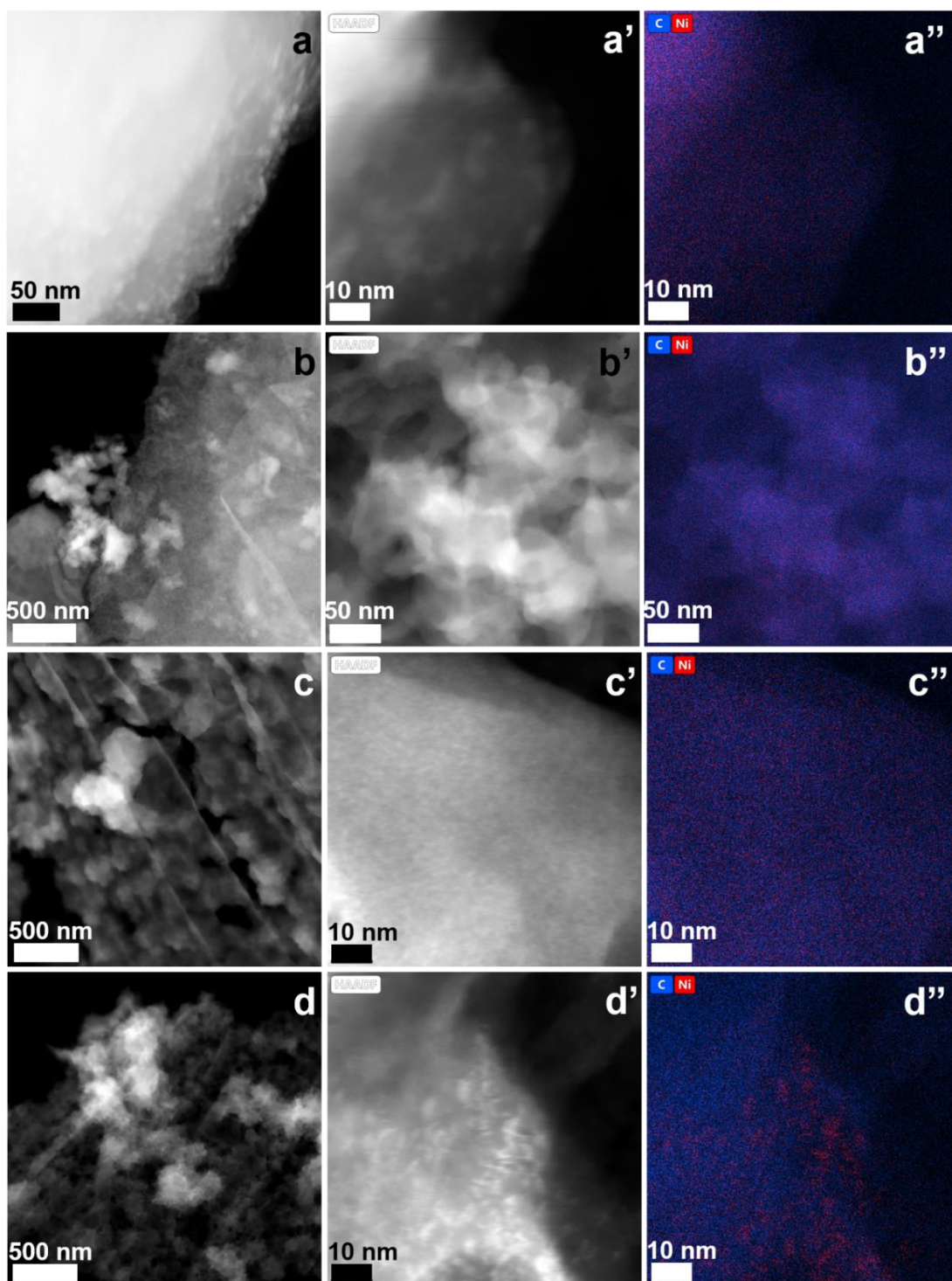
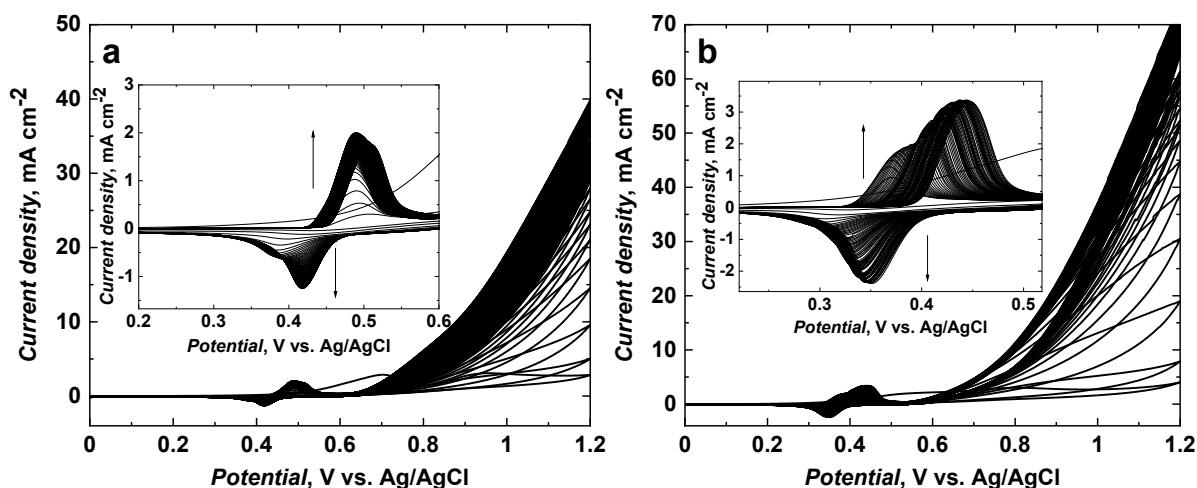


Figure 3.2-5. TEM and HAADF images (a, a', b, b', c, c' and d, d'), and EDX mapping (a'', b'', c'', d'') of (a) poly(NiSaltMe-3dOMe)-PS, (b) poly(NiSaltMe-3dOMe)-PD, (c) poly(*meso*-NiSaldMe-3dOMe)-PS, (d) poly(*meso*-NiSaldMe-3dOMe)-PD.

3.2.4 Potential-driven transformation of poly(NiSalen-3dOMe) precursors into poly[NPs-Ni(OH)₂Salen-3dOMe] catalysts

All poly(NiSalen-3dOMe) precursors were submerged in 0.2 M NaOH_{aq} for their electrochemical transformation into Ni(OH)₂ type NPs.^{9,159} The mechanism of this transformation is already described in Chapter 3.1-2. These transformations were stopped when redox peaks corresponding to the oxidation of poly[NPs-Ni²⁺(OH)₂Salen-3dOMe] to poly(NPs-Ni³⁺OOHSalen-3dOMe) and subsequent reduction back to poly[NPs-Ni²⁺(OH)₂Salen-3dOMe] stabilized (Fig. 3.2-6).

This electrochemical transformation experiment confirmed that poly(*meso*-NiSaldMe-3dOMe) precursors required more CV cycles to transform completely into Ni(OH)₂-type NPs because of the higher electrochemical stability of the polymer, substituted with methyl groups at the imine bridge in the *meso* configuration (Table 3.2-2).¹²⁶ Moreover, precursors deposited under PD conditions also required more CV cycles to generate Ni(OH)₂-type NPs.



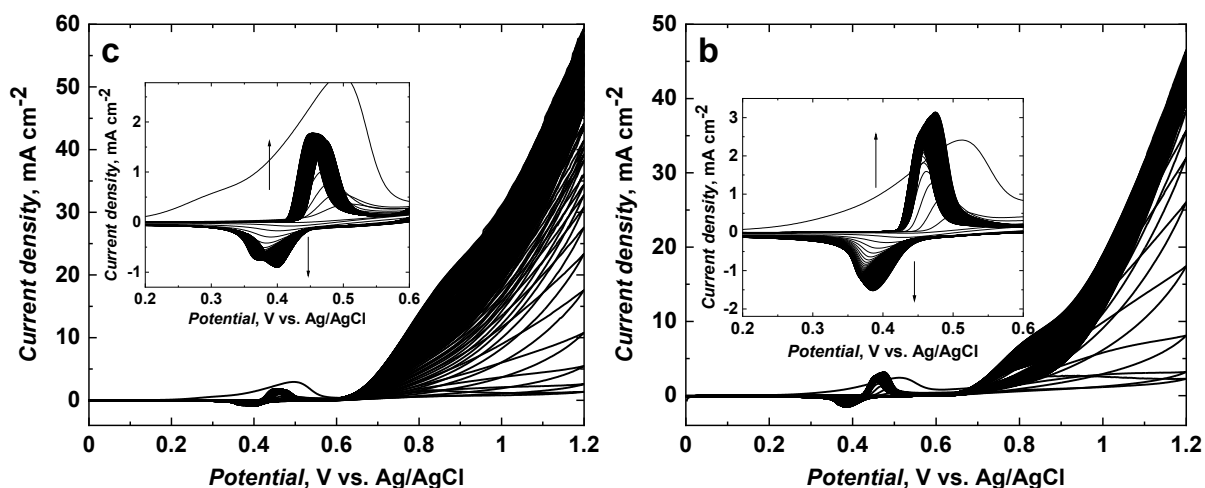


Figure 3.2-6. CV curves recorded during the potential-driven NPs generation from the (a) poly(NiSaltMe-3dOMe)-PD, (b) poly(NiSaltMe-3dOMe)-PS, (c) poly(*meso*-NiSaldMe-3dOMe)-PD, and (d) poly(*meso*-NiSaldMe-3dOMe)-PS. CV was performed at 20 mV s^{-1} in $0.2 \text{ M NaOH}_{\text{aq}}$.

The redox peaks corresponding to the oxidation of poly[NPs- $\text{Ni}^{2+}(\text{OH})_2\text{Salen-3dOMe}$] to poly(NPs- $\text{Ni}^{3+}\text{OOHSalen-3dOMe}$) and subsequent reduction back to poly[NPs- $\text{Ni}^{2+}(\text{OH})_2\text{Salen-3dOMe}$] start to appear at a lower potential in poly(NiSaltMe-3dOMe)-PS, poly(*meso*-NiSaldMe-3dOMe)-PD, and poly(*meso*-NiSaldMe-3dOMe)-PS in comparison to the poly(NiSaltMe-3dOMe)-PD suggesting easier oxidation of such $\text{Ni}(\text{OH})_2$ -type NPs. After the oxidation/reduction peaks of poly[NPs- $\text{Ni}^{2+}(\text{OH})_2\text{Salen-3dOMe}$]/poly(NPs- $\text{Ni}^{3+}\text{OOHSalen-3dOMe}$) appeared, a peak corresponded to OER.¹⁶¹ The separation between these two processes was higher for poly(*meso*-NiSaldMe-3dOMe)-derived catalysts. Moreover, catalysts generated from poly(NiSaltMe-3dOMe)-PS and poly(*meso*-NiSaldMe-3dOMe)-PS showed redox activity at slightly lower potential than that generated from the phenyl ring unsubstituted precursors (Chapter 3.1-2, Fig. 3.1-2), suggesting easier oxidation of $\text{Ni}(\text{OH})_2$ in catalysts generated from substituted precursors deposited under PS conditions.

3.2.5 Morphological characterization of the Ni(OH)₂-type NPs

SEM imaging (Fig. 3.2-7) was used to examine the arrangement of poly(Salen-3dOMe) matrices after the potential-driven transformation step. The poly[NPs-Ni(OH)₂Salen-3dOMe] catalysts were not evenly present on the CP electrode surface. The poly(SaltMe-3dOMe)-PD (Fig. 3.2-7b) matrix exhibited a smooth carbon fiber coating, and during transformation, provided the flattest templating of Ni(OH)₂ NPs. However, this templating remained less uniform than that observed for the phenyl-ring unsubstituted poly(SaltMe) matrix analogs (Chapter 3.1, Fig. 3.1-4). The poly(*meso*-SaldMe-3dOMe)-PS (Fig. 3.2-7c) matrix had a developed surface, and it was the densest. This observation is coherent with the morphology of precursor polymers, where the most pronounced spatial structure was observed in poly(*meso*-NiSaldMe-3dOMe)s. Among the poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe] catalysts (Fig. 3.2-7c, d), the one fabricated from poly(*meso*-NiSaldMe-3dOMe)-PS featured a more 3D globular structure with occasional exposure to bare carbon fiber.

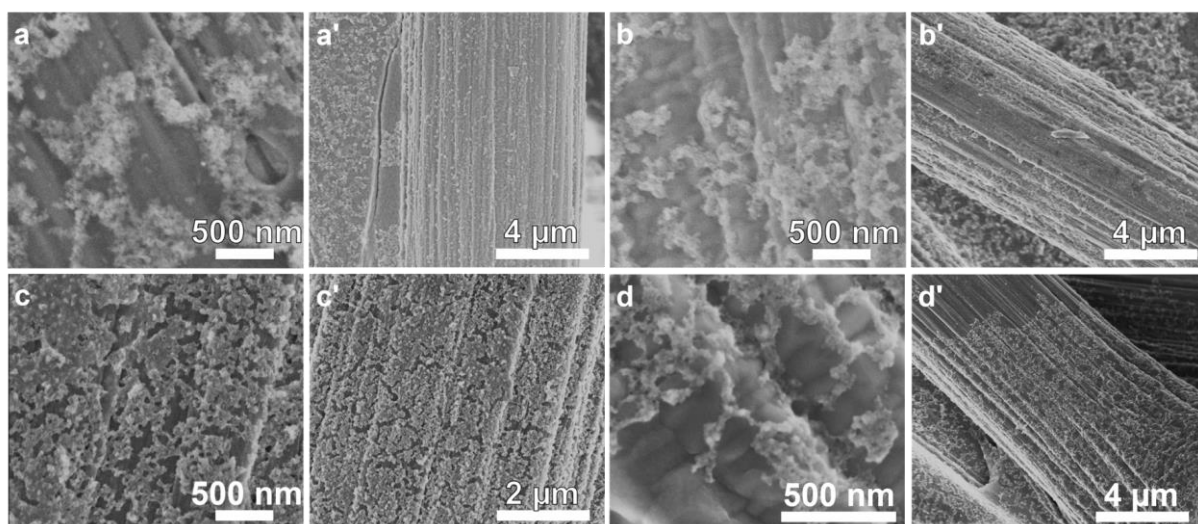


Figure 3.2-7. SEM images of (a, a') poly[NPs-Ni(OH)₂SaltMe-3dOMe]-PS, (b, b') poly[NPs-Ni(OH)₂SaltMe-3dOMe]-PD, (c, c') poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe]-PS, (d, d') poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe]-PD.

TEM imaging (Fig. 3.2-8 and 3.2-9) was employed to examine the distribution of $\text{Ni}(\text{OH})_2$ NPs within the poly(Salen-3dOMe) matrices. The poly[NPs- $\text{Ni}(\text{OH})_2\text{SaltMe-3dOMe}$]-PS catalyst (Fig. 3.2-8a, a', and a'') exhibited a well-distributed NPs arrangement across the matrix; however, a partially overlapping polymer matrix created a misleading appearance of close packing of $\text{Ni}(\text{OH})_2$ -type NPs. The $\text{Ni}(\text{OH})_2$ NPs embedded in poly(SaltMe-3dOMe)-PD matrix (Fig. 3.2-8b) appear bigger than other NPs. For both poly[*meso*-NPs- $\text{Ni}(\text{OH})_2\text{SaltMe-3dOMe}$]-PS (Fig. 3.2-9a, a', and a'') and poly[*meso*-NPs- $\text{Ni}(\text{OH})_2\text{SaltMe-3dOMe}$]-PD (Fig. 3.2-9b, b', and b'') catalysts, the $\text{Ni}(\text{OH})_2$ NPs were spatially distributed throughout the matrix, and the size of NPs was as similar as poly[NPs- $\text{Ni}(\text{OH})_2\text{SaltMe-3dOMe}$]-PD.

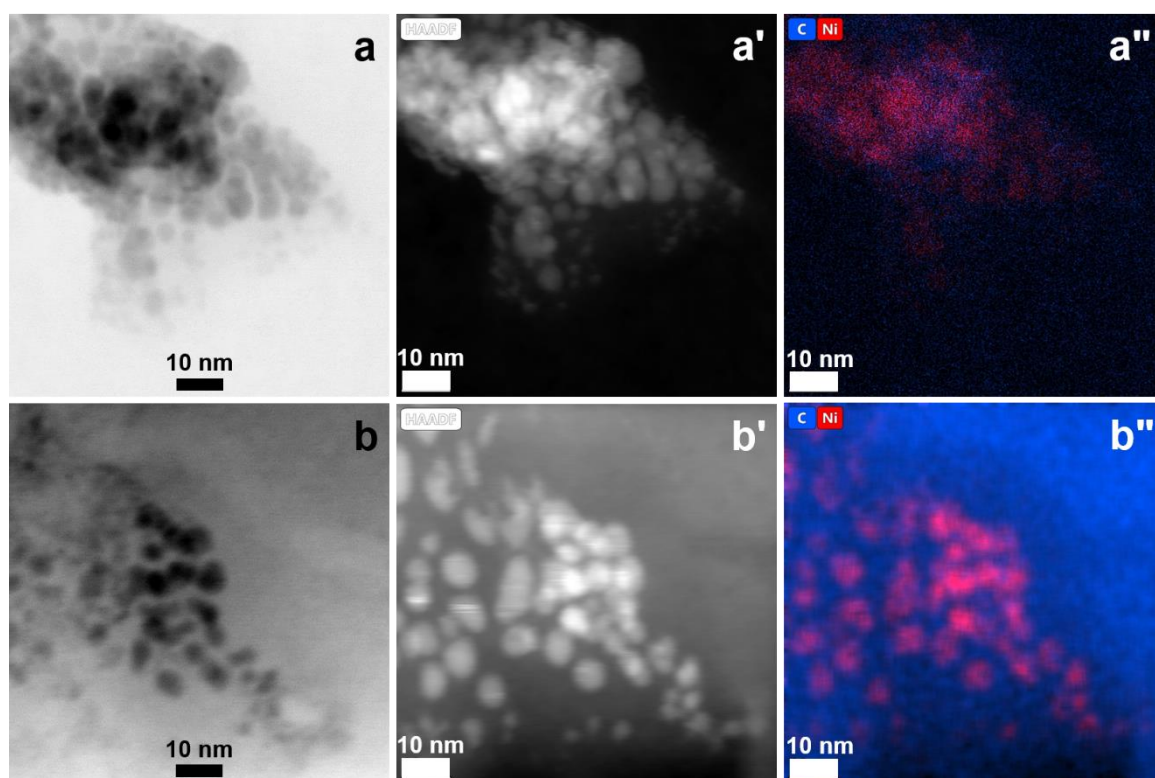


Figure 3.2-8. TEM (a and b), HAADF images (a' and b') and corresponding EDX mapping (a'' and b'') of (a) poly[NPs- $\text{Ni}(\text{OH})_2\text{SaltMe-3dOMe}$]-PS (b) poly[NPs- $\text{Ni}(\text{OH})_2\text{SaltMe-3dOMe}$]-PD.

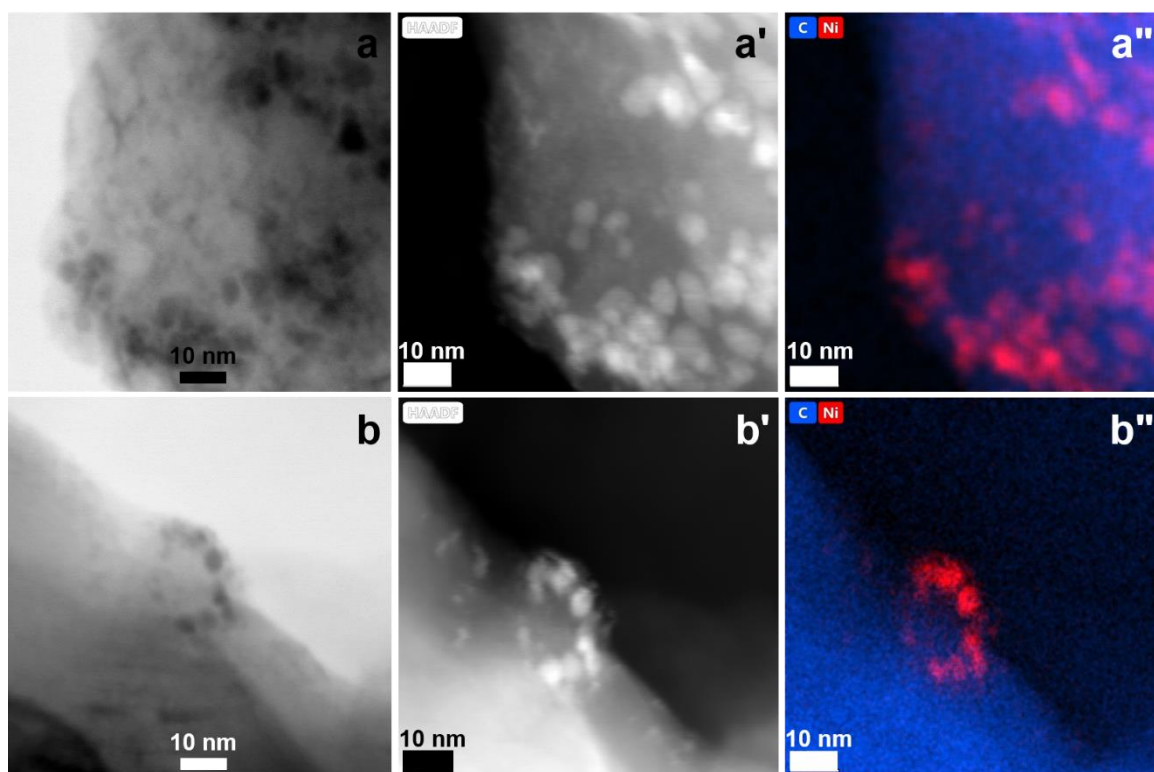


Figure 3.2-9. TEM (a and b), HAADF images (a' and b') and corresponding EDX mapping (a'' and b'') of (a) poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe]-PS (b) poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe]-PD.

3.2.6 Electrocatalytic performance toward ethanol electrooxidation on the poly[NPs-Ni(OH)₂Salen-3dOMe] catalysts

Next, the catalytic activity of the Ni(OH)₂-type NPs derived from substituted poly[NPs-Ni(OH)₂Salen-3dOMe] (Fig. 3.2-10) was examined in the presence of ethanol in 0.2 M NaOH_{aq} in the potential range of 0.0 – 1.0 V vs. Ag/AgCl with a potential scan rate of 50 mV s⁻¹. Both poly[NPs-Ni(OH)₂Salen-3dOMe] catalysts exhibited a linear increase of electrocatalytic activity in the ethanol concentration range of 0.05 – 0.5 M. The electrocatalytic efficiency was higher for catalysts derived from poly(*meso*-NiSaldMe-3dOMe) precursor, reaching 87.3 and 85.3 mA cm⁻² M⁻¹ for poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe]-PS and poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe]-PD, respectively. The highest electrocatalytic activity obtained for the

poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe]-PS was consistent with SEM imaging (Fig. 3.2-7), where the poly(*meso*-SaldMe-3dOMe)-PS (Fig. 3.2-7c) matrix had the most developed surface. A slightly lower electrocatalytic efficiency of 83.2 mA cm⁻² M⁻¹ was obtained for poly[NPs-Ni(OH)₂SaltMe-3dOMe]-PS. In contrast, a markedly lower catalytic efficiency (44.1 mA cm⁻² M⁻¹) was observed for poly[NPs-Ni(OH)₂SaltMe-3dOMe]-PD catalyst, which is consistent with TEM observations where a relatively low Ni content was observed in the corresponding poly(NiSaltMe-3dOMe)-PD precursor.

One of the most important conclusions that can be drawn from these results is that catalytic activities recorded on Ni(OH)₂-type NPs derived from substituted poly(NiSalen-3dOMe) precursors are higher than those for Ni(OH)₂-type NPs derived from unsubstituted in the phenyl ring poly(NiSalen) precursors (Chapter 3.1). This can be attributed to the arrangement of Ni(OH)₂ NPs within the matrices. The phenyl-ring substituted poly(Salen-3dOMe) matrices templated Ni(OH)₂ NPs in a more spatially diverse manner; even in the case of the poly(SaltMe-3dOMe) matrix, spatial templating was observed. This, in turn, leads to the increased electrocatalytic efficiency of the poly[NPs-Ni(OH)₂Salen-3dOMe] catalysts.

Table 3.2-2. Efficiency of electrooxidation of ethanol over poly[NPs-Ni(OH)₂Salen-3dOMe] catalysts.

electrodeposition conditions	Poly[NPs-Ni(OH) ₂ SaltMe-3dOMe]		Poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe-3dOMe]	
	Number of cycles for NPs generation	Sensitivity mA cm ⁻² M ⁻¹	Number of cycles for NPs generation	Sensitivity mA cm ⁻² M ⁻¹
PS	102	83.2	150	87.3
PD	151	44.1	200	85.3

The ethanol electrooxidation on the poly[NPs-Ni(OH)₂Salen-3dOMe] catalysts proceeds *via* an EC' mechanism, the same as for unsubstituted poly[NPs-Ni(OH)₂Salen] catalysts. This

mechanism is described in detail in Chapter 3.1.10. The electrocatalysis for substituted poly[NPs-Ni(OH)₂Salen-3dOMe] catalysts occurred according to Equations 3.2-1 and 3.2-2:

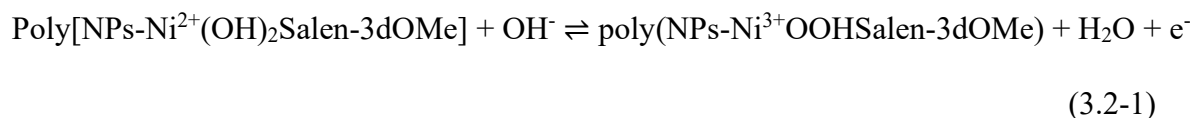
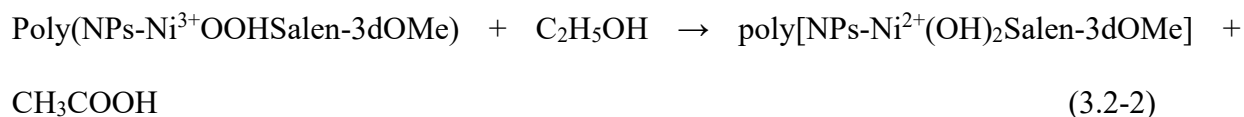
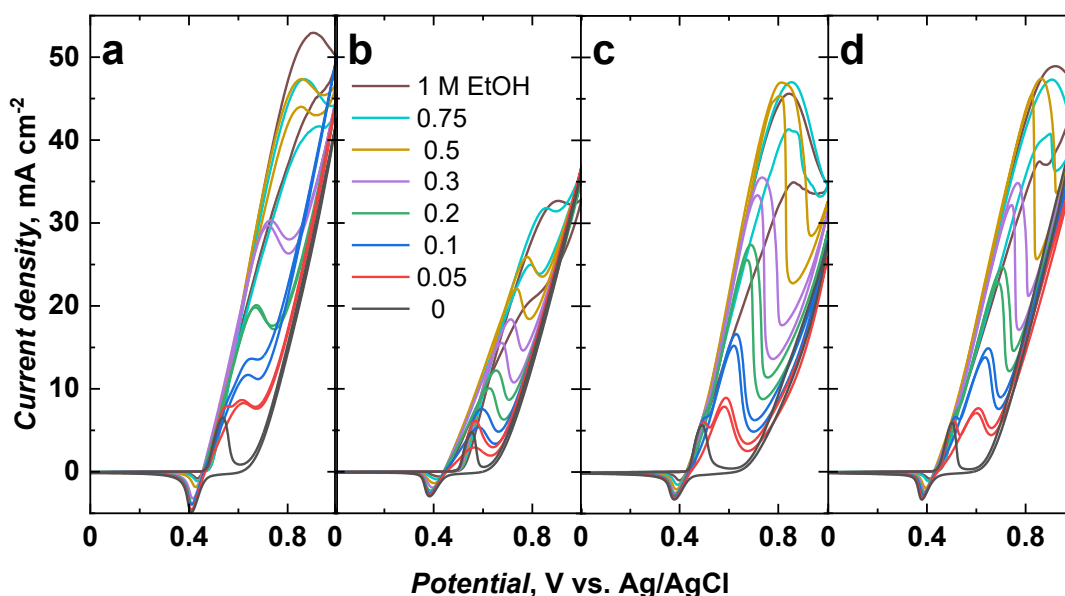


Figure 3.2-10. Catalytic CV responses of (a) poly[NPs-Ni(OH)₂SaltMe-3dOMe]-PS, (b) poly[NPs-Ni(OH)₂SaltMe-3dOMe]-PD, (c) poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe]-PS, and (d) poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe]-PD toward various ethanol concentrations. CVs were performed at 50 mV s⁻¹ in 0.2 M NaOH_{aq}.

A closer look at the catalytic current measured in the presence of ethanol (Fig. 3.2-11) showed that the catalytic current recorded at poly[NPs-Ni(OH)₂SaltMe-3dOMe]-PS in forward and backward scans was nearly identical. In contrast, anodic currents measured at poly[NPs-

Ni(OH)₂SaltMe-3dOMe]-PD in the forward and backward direction were unequal, suggesting incomplete generation of catalytically active centers. Interestingly, poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe]-PS, and poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe]-PD catalysts had well separated OER and EOR peaks and catalytic current similar to that for poly[NPs-Ni(OH)₂SaltMe-3dOMe]-PS. However, the current measured during the backward scan was slightly lower than that during the forward scan, suggesting that the electrooxidation products were partially adsorbed, blocking active sites and limiting further catalytic activity.

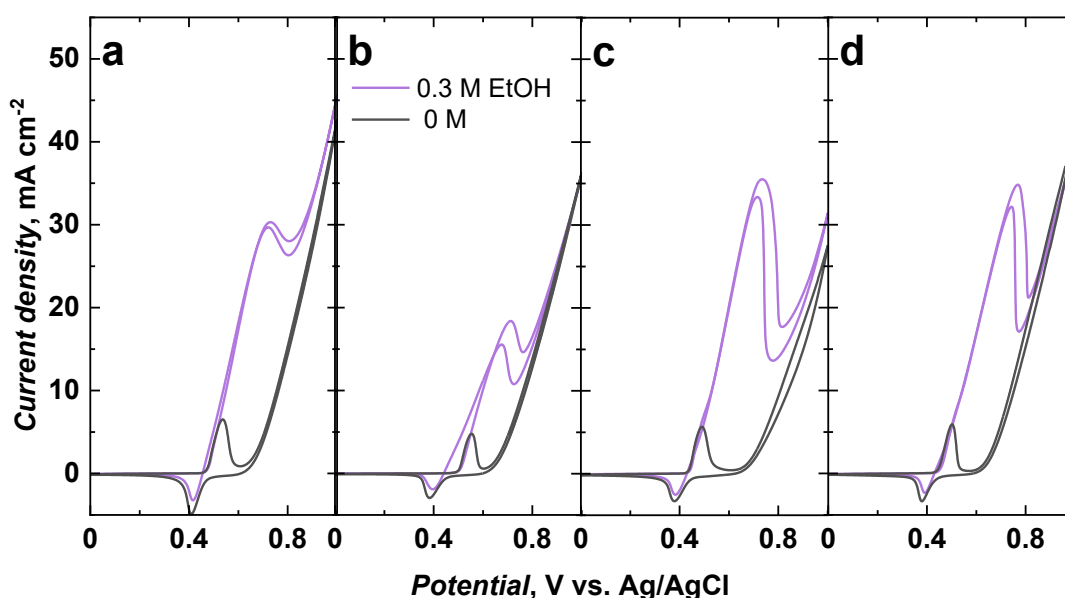


Figure 3.2-11. Catalytic CV responses of (a) poly[NPs-Ni(OH)₂SaltMe-3dOMe]-PS, (b) poly[NPs-Ni(OH)₂SaltMe-3dOMe]-PD, (c) poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe]-PS, and (d) poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe]-PD toward 0.3 M ethanol. CVs were performed at 50 mV s⁻¹ in 0.2 M NaOH_{aq}.

There are limited methodologies available for preparing Ni-based catalysts. Most of these catalysts are prepared *via* time-consuming hydro- and solvothermal processes, followed by high-temperature treatments, both of which require significant energy. In contrast, the approach presented in Chapters 3.1 and 3.2 enables the facile, energy-efficient, and reproducible

fabrication of electrocatalysts with excellent electrochemical performance. The achieved current densities are higher than those reported for similar materials (Table 3.2-3). This is due to the uniform distribution of NPs in the polymer matrix. Moreover, among catalysts presented in this thesis, poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe]-PS exhibited a higher current density than poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low} (Table 3.2-3).

Table 3.2-3. Comparison of electrocatalytic activity of NiSalen-based materials toward ethanol electrooxidation.

Substrate	C _{NaOH} M	C _{EtOH} M	Current density (maximal) mA cm ⁻²	Scan rate mV s ⁻¹	Ref.
Poly[Ni(Salen)]/GCE	1.0	0.1	16.5	50	60
Poly[Ni(3-MeOSalen)]-GCE	0.2	1.0	10	50	61
Poly[Ni(α,α' -methyl ₂ salen)]/GCE	0.1	0.3	15	50	62
Poly[Ni(II)-DHS]/GCE	0.1	0.1	2.5	20	64
Poly[VP- <i>co</i> -DVB-Ni(II)]/CE	0.5	1.0	~0.35	15	41
Ni ^{II} -Zeolite-Y/CE	1.0	0.49	6.2	20	11
Poly[Ni ^{II}]/Pt	1.0	0.12	~23.5	20	11
[Ni(cis-salen)]/CPE	1.0	0.5	~1.6 mA*	50	175
Poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe]-PS _{low} **/CPE	0.2	0.3	29.6	50	Reported in this thesis (Chapter 3.1)
Poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe-3dOMe]-PS/CPE	0.2	0.3	35.5	50	Reported in this thesis (This Chapter)

GCE – glassy carbon electrode, CE – carbon paste electrode, CPE – carbon paper electrode, VP-*co*-DVB – 4-vinylpyridine-*co*-divinylbenzene, Pt- platinum

*The original article did not provide the area of the working electrode.

**PS_{low} refers to the sample derived from the polymer deposited with a charge of 137.1 mC cm⁻².

3.3 Optimizing the morphology of poly[NPs-Ni(OH)₂-Salen] electrocatalyst and electrocatalysis conditions for effective urea remediation

This chapter discusses the research work published in *Catal. Sci. Technol.*, 2025,15, 794-807.

In this study, generation conditions for poly[NPs-Ni(OH)₂SaltMe] and poly[*meso*-NPs-Ni(OH)₂SaldMe] catalysts were optimized to obtain Ni(OH)₂-type NPs with suitable morphology, resistant to poisoning, and having active sites with the highest *in situ* generation ability. Later, electrochemical experimental conditions were optimized to determine suitable operating conditions for poly[NPs-Ni(OH)₂Salen] catalysts. Parameters, such as activation energy and Tafel slopes, were calculated to compare the catalytic performance of differently generated NPs.

Different NPs samples were generated from PS-deposited poly(NiSalen) precursors *via* potential-driven transformation at different NaOH_{aq} concentrations. This approach enabled the fabrication of catalysts with diverse morphological structures. The electrocatalytic performance of such fabricated catalysts toward urea electrooxidation was evaluated in various NaOH_{aq} concentrations. To demonstrate the utility of poly[NPs-Ni(OH)₂Salen] catalysts for the remediation of urea-rich wastewater, a durability test of electrocatalysts in the real system mimicking conditions was performed.

3.3.1 Potential-driven transformations of poly(NiSalen)₁₃₀ precursors into the poly[NPs-Ni(OH)₂Salen] catalysts

The study began with the optimization of the conditions for generating poly[NPs-Ni(OH)₂Salen] electrocatalyst. To achieve this, firstly, poly(NiSalen)s were electrodeposited from an ACN solution containing 1 mM of either NiSaltMe or *meso*-NiSaldMe monomers and 0.1 M (TBA)PF₆ as the supporting electrolyte. A constant potential of 1.3 V vs. Ag/Ag⁺ was applied until a total charge of 130 mC cm⁻² was achieved (Fig. 3.3-1). This way, poly(NiSaltMe)₁₃₀ and poly(*meso*-NiSaldMe)₁₃₀ precursors were prepared. These precursors were subsequently transferred into 0.2, 0.5, 1.0, and 2.0 M NaOH aqueous solutions to conduct potential-driven transformation within a potential window of 0.0 – 1.2 V vs. Ag/AgCl (3 M KCl) at a scan rate of 20 mV s⁻¹. Cycling was continued until the redox peaks of Ni²⁺↔Ni³⁺ stabilized. This resulted in the formation of eight different electrocatalysts, named as follows:

- | | |
|--|--|
| 1. poly[NPs-Ni(OH) ₂ SaltMe] _{0.2 M} , | 5. poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe] _{0.2 M} , |
| 2. poly[NPs-Ni(OH) ₂ SaltMe] _{0.5 M} , | 6. poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe] _{0.5 M} , |
| 3. poly[NPs-Ni(OH) ₂ SaltMe] _{1.0 M} , | 7. poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe] _{1.0 M} , |
| 4. poly[NPs-Ni(OH) ₂ SaltMe] _{2.0 M} , | 8. poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe] _{2.0 M} . |

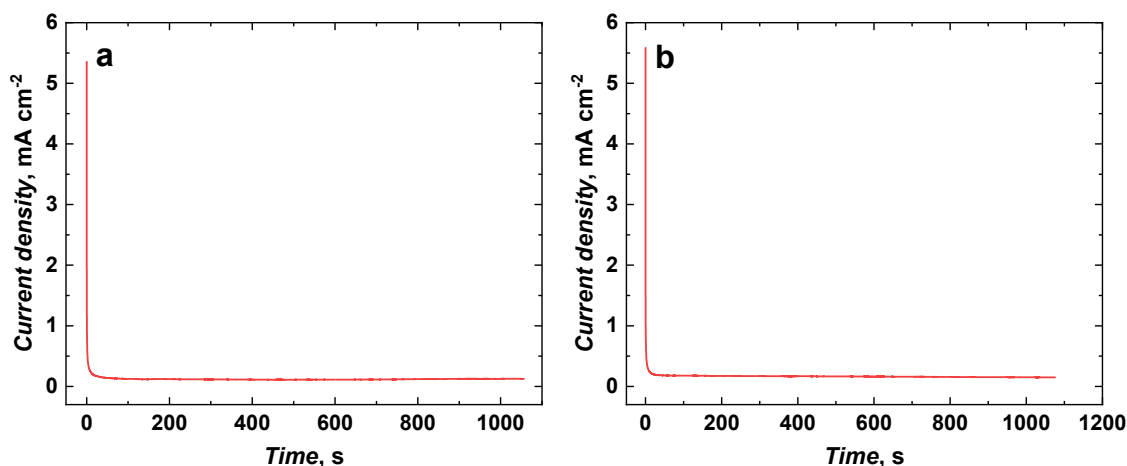


Figure 3.3-1. PS depositions of (a) poly(NiSaltMe)₁₃₀ and (b) poly(*meso*-NiSaldMe)₁₃₀ by applying a constant potential of 1.3 V vs. Ag/Ag⁺ until 130 mC cm⁻² charge was reached.

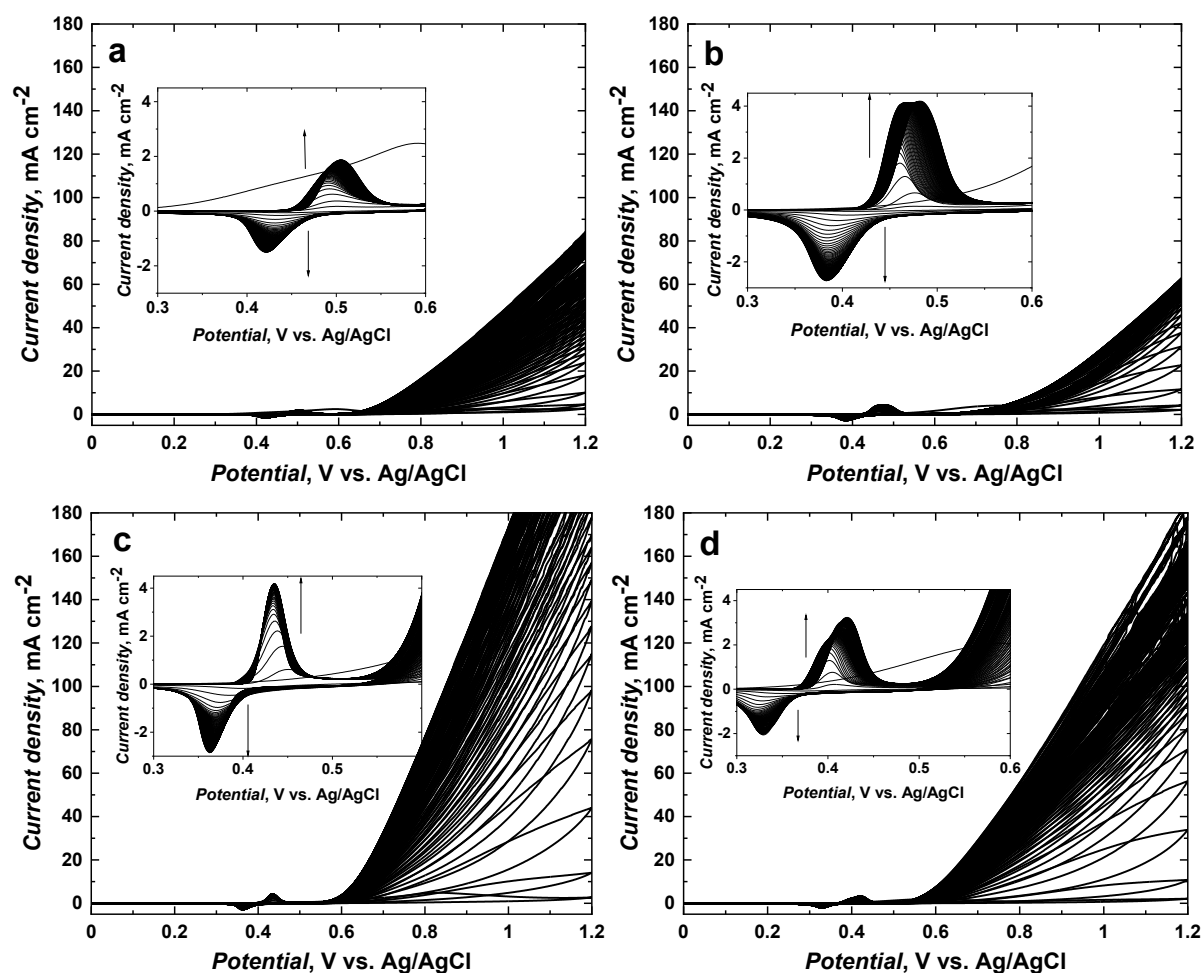


Figure 3.3-2. Multiple CV curves performed in (a) 0.2 M NaOH_{aq}, (b) 0.5 M NaOH_{aq}, (c) 1.0 M NaOH_{aq}, and (d) 2.0 M NaOH_{aq} at 20 mV s⁻¹, showing the potential-driven transformation of poly(NiSaltMe)₁₃₀ into poly[NPs-Ni(OH)₂SaltMe] catalysts.

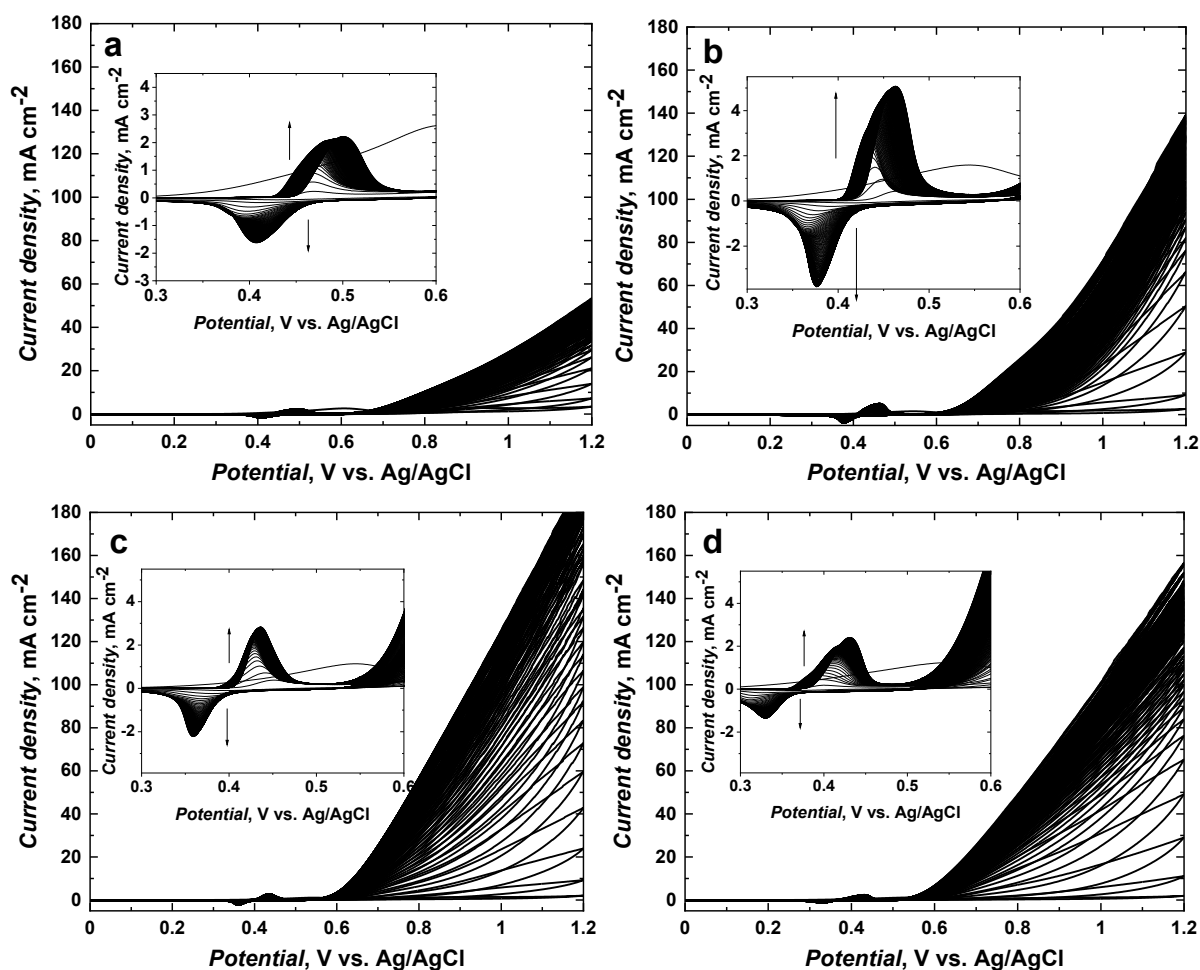


Figure 3.3-3. Multiple CV curves performed in (a) 0.2 M NaOH_{aq}, (b) 0.5 M NaOH_{aq}, (c) 1.0 M NaOH_{aq}, and (d) 2.0 M NaOH_{aq} at 20 mV s⁻¹, showing the potential-driven transformation of poly(*meso*-NiSaldMe)₁₃₀ into poly[*meso*-NPs-Ni(OH)₂SaldMe] catalysts.

The slow but successful transformation of poly(NiSalen)₁₃₀ precursors into poly[NPs-Ni(OH)₂Salen] electrocatalysts was evidenced by the growth of the Ni²⁺(OH)₂/Ni³⁺OOH redox peaks (Fig. 3.3-2 and 3.3-3). In this potential-driven process, cleavage of Ni-N bonds happens due to axial coordination of the OH⁻ to the Ni²⁺ center, a key step. Therefore, investigating the effect of NaOH_{aq} concentration on the transformation duration and efficiency is essential. However, the number of cycles required for complete potential-driven transformation did not depend on the NaOH_{aq} concentration, and increasing the NaOH_{aq} concentration did not shorten the generation process (Table 3.3-1). Conversely, the NaOH_{aq} concentration significantly

influenced the number of active sites, as indicated by the highest reduction peak obtained for the transformation carried out in 1.0 M NaOH_{aq} (Fig. 3.3-4, blue curves). Besides, the poly[NPs-Ni²⁺(OH)₂Salen]/(NPs-Ni³⁺OOHSalen) oxidation/reduction occurred at a lower potential in higher NaOH_{aq} concentrations (Fig. 3.3-4). It is anticipated that the differences visualized in the last CV cycle of measurements, performed in different NaOH_{aq} concentrations, are related to potential-induced cleavage of the bonds between nitrogen belonging to imine moieties and Ni²⁺ occurring in bulk and on the surface for poly(*meso*-NiSaldMe)₁₃₀ and poly(NiSaltMe)₁₃₀, respectively. At moderately high NaOH_{aq} concentration, cleavage of those bonds was easy and happened at a lower overpotential.

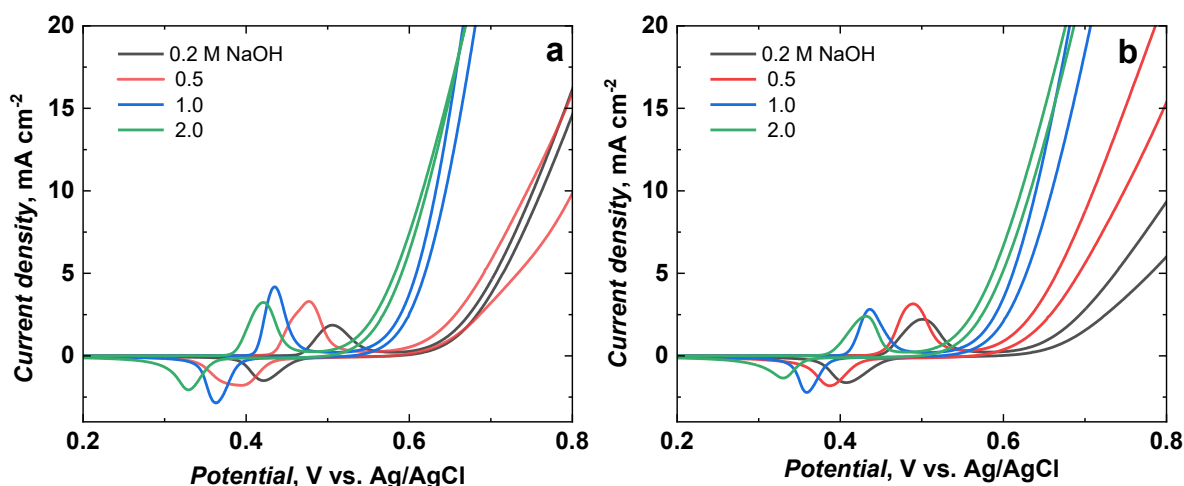


Figure 3.3-4. The last CV cycle of the potential-driven transformation of (a) poly(NiSaltMe)₁₃₀ and (b) poly(*meso*-NiSaldMe)₁₃₀ into the poly[NPs-Ni(OH)₂Salen] catalysts, performed in 0.2, 0.5, 1.0, and 2.0 M NaOH_{aq} concentrations.

Table 3.3-1. Number of CV cycles performed to fully generate poly[NPs-Ni(OH)₂Salen] catalysts in different NaOH_{aq} concentrations.

$C_{\text{NaOH}_{\text{aq}}}$ (M)	Poly[NPs-Ni(OH) ₂ SaltMe] ₁₃₀	Poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe] ₁₃₀
	Number of required CV cycles	
0.2	120	150
0.5	100	150
1.0	130	130
2.0	130	150

3.3.2 Poly[NPs-Ni(OH)₂Salen] catalysts morphology study

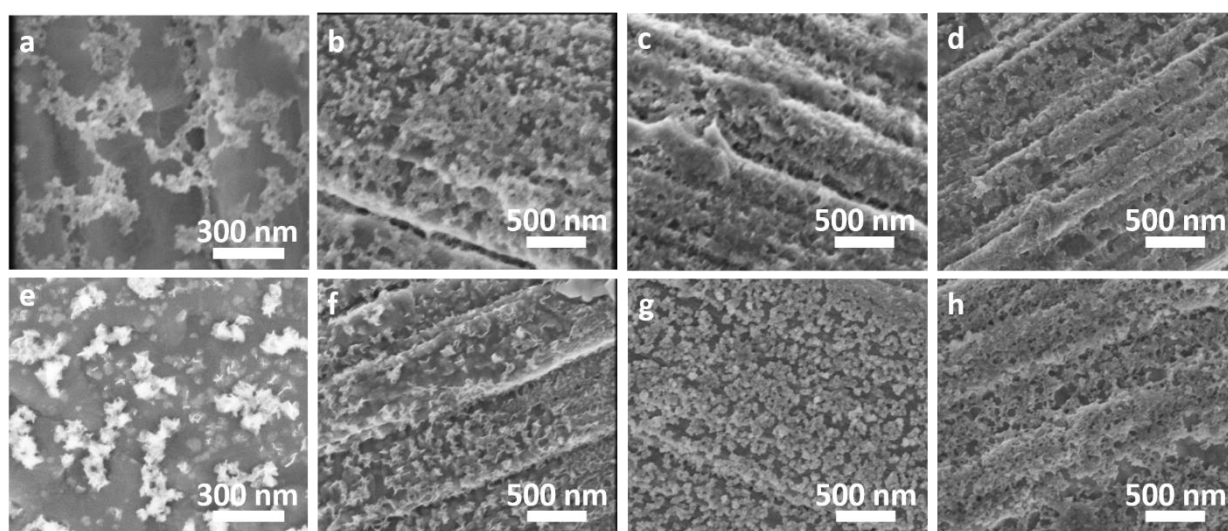


Figure 3.3-5. SEM images of poly[NPs-Ni(OH)₂SaltMe] (a, b, c, d) and poly[*meso*-NPs-Ni(OH)₂Salen] (e, f, g, h) electrocatalysts, derived in (a, e) 0.2 M NaOH_{aq}, (b, f) 0.5 M NaOH_{aq}, (c, g) 1.0 M NaOH_{aq}, and (d, h) 2.0 M NaOH_{aq}.

The morphological differences between poly[NPs-Ni(OH)₂SaltMe] and poly[*meso*-NPs-Ni(OH)₂SaldMe] catalysts prepared in different NaOH_{aq} concentrations were investigated using SEM imaging (Fig. 3.3-5). As discussed in Chapter 3.1, the deposition conditions

influenced the morphology of the poly(NiSalen) precursors, which in turn affected the structural arrangement of the resulting poly[NPs-Ni(OH)₂Salen] catalysts.

In this study, precursors deposited at the same potential and charge were potentially driven to transform into Ni(OH)₂-type NPs in varying NaOH_{aq} concentrations. That led to differences in the spatial arrangement of the final catalysts. The poly(SaltMe) matrix exhibited a compact, planar arrangement (Fig. 3.3-5a, b, c, and d). In contrast, the poly(*meso*-SaldMe) matrix showed a more spatially diversified, three-dimensional structure (Fig. 3.3-5e, f, g, and h).

The poly(SaltMe) matrices served as a planar 2D template for the Ni(OH)₂ NPs (Fig. 3.3-5a, b, c, and d). The NaOH_{aq} concentration used during the transformation strongly influenced the matrix packing density after NPs generation. At lower NaOH_{aq} concentrations (0.2 and 0.5 M), uncoated areas of the carbon fiber substrate were visible (Fig. 3.3-5a and b). In contrast, at higher NaOH_{aq} concentrations (1.0 and 2.0 M), the flake-shaped 2D poly(SaltMe) matrix completely covered the carbon fibers (Fig. 3.3-5c and d).

Whereas the poly(*meso*-SaldMe) matrix appeared 3D. The spatially diversified structure was loosely packed in the sample generated from lower NaOH_{aq} concentrations (0.2 and 0.5 M) (Fig. 3.3-5e and f). At higher NaOH_{aq} concentrations (1.0 and 2.0 M), the 3D matrix achieved more uniform coverage on the carbon fibers (Fig. 3.3-5g and h). Markedly, the spacing between poly(*meso*-SaldMe) matrix parts appeared optimally balanced, neither merged nor separated, for the catalysts derived in the 1.0 M NaOH_{aq} (Fig. 3.3-5g).

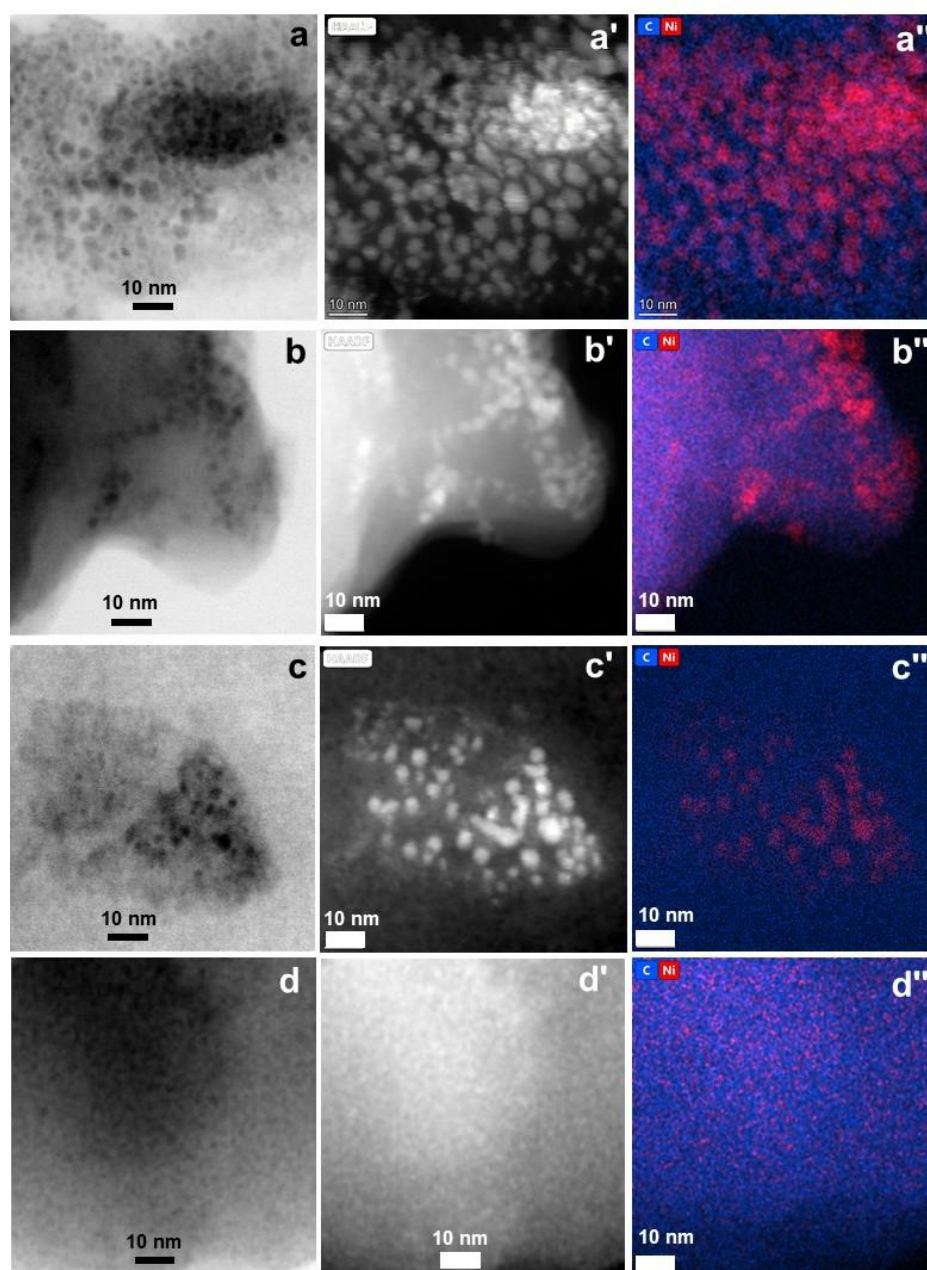


Figure 3.3-6. TEM (a, b, c and d), HAADF images (a', b', c' and d') and corresponding EDX mapping (a'', b'', c'' and d'') of electrocatalysts (a) poly[NPs-Ni(OH)₂SaltMe]_{0.2 M}, (b) poly[NPs-Ni(OH)₂SaltMe]_{0.5 M}, (c) poly[NPs-Ni(OH)₂SaltMe]_{1.0 M}, and (d) poly[NPs-Ni(OH)₂SaltMe]_{2.0 M}. EDX profiles for carbon (blue) and Ni (red).

The nanoscale size of the Ni(OH)₂ particles was confirmed by TEM imaging (Fig. 3.3-6 and 3.3-7). Additionally, EDX mapping confirmed that the nanoscale objects were composed of C (blue) and Ni (red) and corresponded to Ni(OH)₂-type NPs (Fig. 3.3-6 and 3.3-7). The

differences in $\text{Ni}(\text{OH})_2$ -type NPs distribution and matrix separation originated from the unlike spatial arrangements of poly(SaltMe) and poly(*meso*-SaldMe), as visualized by SEM (Fig. 3.3-5).

The size of $\text{Ni}(\text{OH})_2$ NPs embedded in the poly(SaltMe) matrix was smaller than 5 nm (Fig. 3.3-6a, a'). Overlapping polymer matrix partially created a misleading appearance of NPs aggregation in some images (Fig. 3.3-6a, a'). Notably, smaller NPs were observed in higher NaOH_{aq} concentrations (Fig. 3.3-6b, c), and for the 2.0 M NaOH_{aq} (Fig. 3.3-6d), the NPs size dropped below 2 nm. This suggested that the $\text{Ni}(\text{OH})_2$ -type NPs might be chemically unstable in highly alkaline conditions.

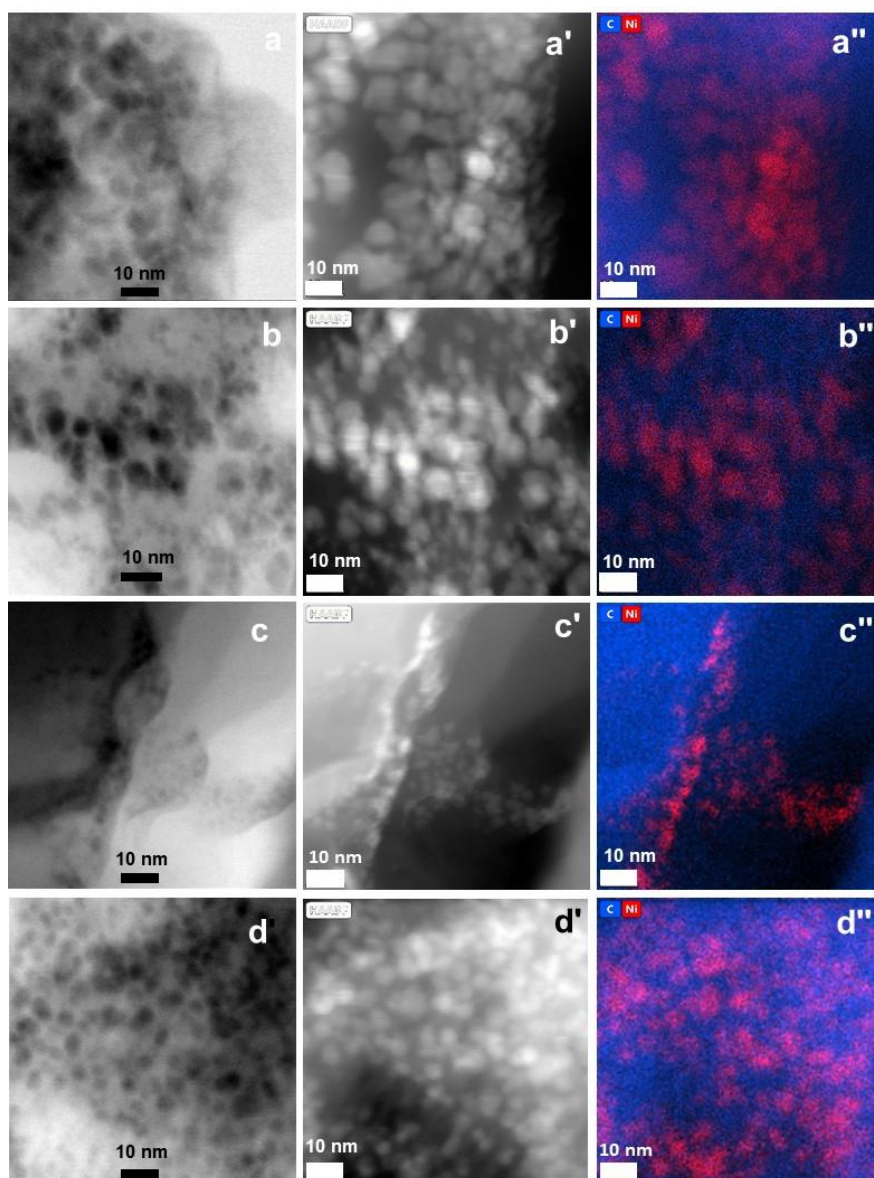


Figure 3.3-7. TEM (a, b, c, and d), HAADF images (a', b', c', and d'), and corresponding EDX mapping (a'', b'', c'', and d'') of electrocatalysts (a) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{0.2 M}, (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{0.5 M}, (c) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M}, and (d) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{2.0 M}. EDX profiles for carbon (blue) and Ni (red).

The poly[*meso*-NPs-Ni(OH)₂SaldMe] catalysts fabricated in different NaOH_{aq} concentrations had various sizes. Ni(OH)₂-type NPs generated in 0.2 and 0.5 M NaOH_{aq} (Fig. 3.3-7a, b) were slightly bigger than those generated in 1.0 and 2.0 M NaOH_{aq} (Fig. 3.3-6c, d). When comparing the Ni(OH)₂-type NPs sizes based on the precursor poly(NiSalen) used, the NPs derived from

poly(*meso*-NiSaldMe) precursors (Fig. 3.3-7) were generally larger than those generated from poly(NiSaltMe) precursors (Fig. 3.3-6). Even after the potential-driven generation performed at 2.0 M NaOH_{aq}, the Ni(OH)₂-type NPs remained visible (Fig. 3.3-7d), indicating that Ni(OH)₂ NPs embedded in poly(*meso*-SaldMe) matrices were stable.

3.3.3 Optimization of the catalyst preparation conditions

The electrocatalytic responses of poly[NPs-Ni(OH)₂SaltMe] and poly(*meso*-NPs-Ni(OH)₂SaldMe] catalysts, generated in 0.2, 0.5, 1.0, and 2.0 M NaOH_{aq}, were registered in the presence of 0.01, 0.05, 0.1, 0.3, and 0.5 M urea. Each electrocatalyst was tested at the same NaOH_{aq} concentration used during its generation; i.e., the responses of poly[NPs-Ni(OH)₂SaltMe]_{0.2 M} were recorded in 0.2 M NaOH_{aq}. During this experiment, urea was added to the electrochemical cell in two ways:

- (i) Separately – each measurement was conducted in a fresh urea solution of different concentrations.
- (ii) Continuously – each measurement was performed in the same solution, where an appropriate amount of urea was added to obtain the desired concentration.

This was done to avoid the effect of a change in urea concentration resulting from urea consumption during electrooxidation. Moreover, continuous measurement could reveal the impact of electrochemical oxidation product accumulation. When the urea portions were added separately, the issue of product accumulation was excluded. Using both methods of urea addition to the cell allowed a comparative analysis of each catalyst's resistance to poisoning by urea electrooxidation products.

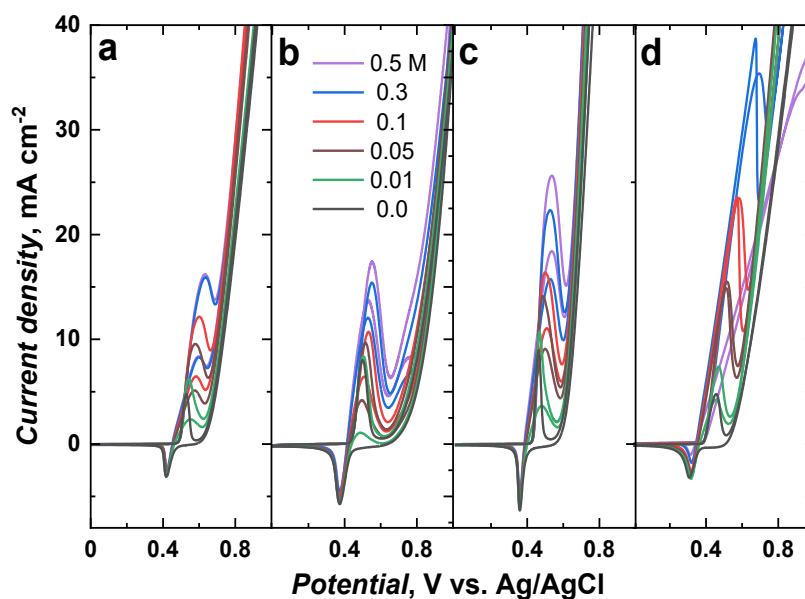


Figure 3.3-8. The catalytic CV responses of (a) poly[NPs-Ni(OH)₂SaltMe]_{0.2 M} (b) poly[NPs-Ni(OH)₂SaltMe]_{0.5 M}, (c) poly[NPs-Ni(OH)₂SaltMe]_{1.0 M}, and (d) poly[NPs-Ni(OH)₂SaltMe]_{2.0 M} catalysts toward the urea electrooxidation. Urea was added separately to the cell. The CVs were registered in (a) 0.2 M NaOH_{aq}, (b) 0.5 M NaOH_{aq}, (c) 1.0 M NaOH_{aq}, and (d) 2.0 M NaOH_{aq} with the scan rate of 50 mV s⁻¹.

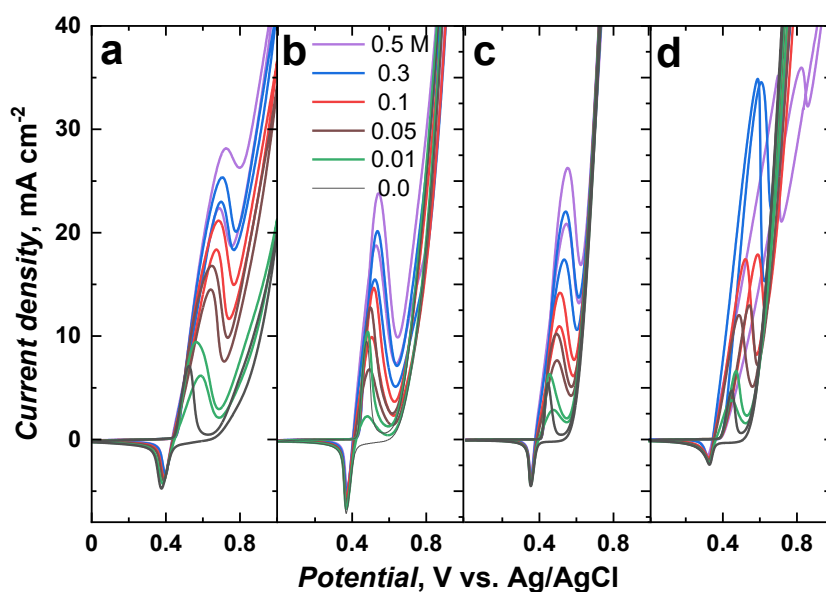
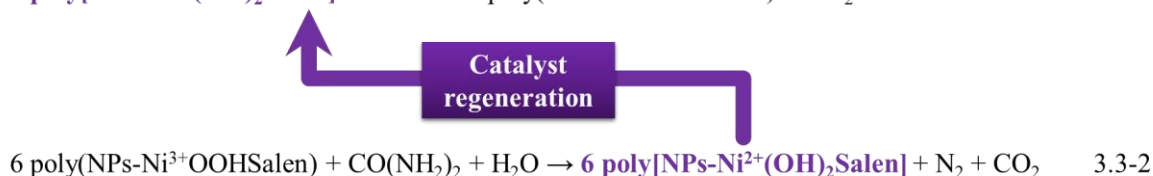


Figure 3.3-9. The electro-catalytic CV responses of (a) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{0.2 M}, (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{0.5 M}, (c) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M}, and (d) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{2.0 M} catalysts toward the urea electrooxidation. Urea was added separately to the cell. The CVs were registered in (a) 0.2 M NaOH_{aq}, (b) 0.5 M NaOH_{aq}, (c) 1.0 M NaOH_{aq}, and (d) 2.0 M NaOH_{aq} with the scan rate of 50 mV s⁻¹.

The electrocatalytic CV responses of the poly[NPs-Ni(OH)₂Salen] catalyst in pure NaOH_{aq} are presented as black curves in Figures 3.3-8, 3.3-9, 3.3-10, and 3.3-11. These CV responses showed typical electrooxidation and electroreduction peaks corresponding to the redox couple of poly[NPs-Ni²⁺(OH)₂Salen]/poly(NPs-Ni³⁺OOHSalen).⁶² The potential of this redox pair was dependent on the NaOH_{aq} concentration. The redox peak potentials shifted to lower values as the NaOH_{aq} concentration increased. Beyond ~0.75 V, a rise in current was observed because of the onset of the OER¹⁷⁶.

In the presence of urea, all poly[NPs-Ni(OH)₂Salen] catalysts oxidized urea *via* the indirect mechanism.^{61,82,121} In this process, urea is oxidized at the gradually electrogenerated (Equation 3.3-1), accessible, and catalytically active poly(NPs-Ni³⁺OOHSalen) centers. These active sites mediate the chemical oxidation of urea into CO₂ and N₂. (Equation 3.3-2). Simultaneously, the poly(NPs-Ni³⁺OOHSalen) centers are reduced back to poly[NPs-Ni(OH)₂Salen], a process defined as a catalyst regeneration. During the overall process, this catalyst regeneration can decrease the amount of poly(NPs-Ni³⁺OOHSalen) active centers.



In the case of separately added urea, CV curves exhibited an increase in current during the forward scan, demonstrating urea oxidation at the poly(NPs-Ni³⁺OOHSalen) active sites (Fig. 3.3-8 and 3.3-9). At higher potentials, this current decreased due to the reduction of these active sites back to the poly[NPs-Ni²⁺(OH)₂Salen] during the chemical oxidation of urea. Through backward potential scan, a second oxidation peak appeared at potentials favorable for urea electrooxidation. This was possible because the poly(NPs-Ni³⁺OOHSalen) active sites were generated again during the reverse scan. The higher backward peak suggested better

electrocatalytic performance of the electrocatalyst due to its high durability and fast generation ability of poly(NPs-Ni³⁺OOHSalen) centers.

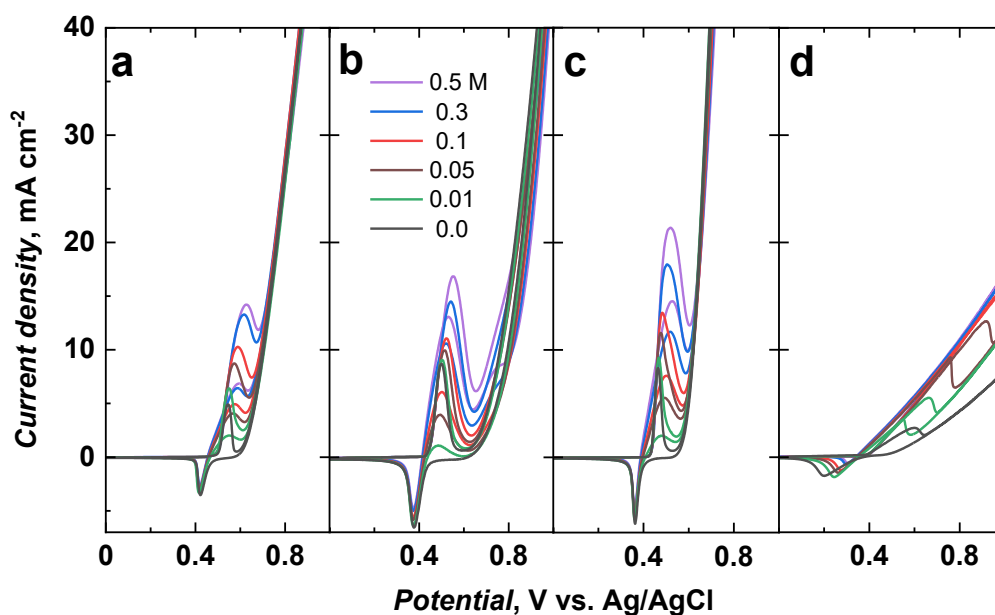


Figure 3.3-10. The electrocatalytic CV responses of (a) poly[NPs-Ni(OH)₂SaltMe]_{0.2 M}, (b) poly[NPs-Ni(OH)₂SaltMe]_{0.5 M}, (c) poly[NPs-Ni(OH)₂SaltMe]_{1.0 M}, and (d) poly[NPs-Ni(OH)₂SaltMe]_{2.0 M} toward urea electrooxidation. The CVs were registered with the scan rate of 50 mV s⁻¹ in (a) 0.2 M NaOH_{aq}, (b) 0.5 M NaOH_{aq}, (c) 1.0 M NaOH_{aq} and (d) 2.0 M NaOH_{aq}. Urea was added continuously in the electrochemical cell after each electrocatalysis step to reach the desired concentration.

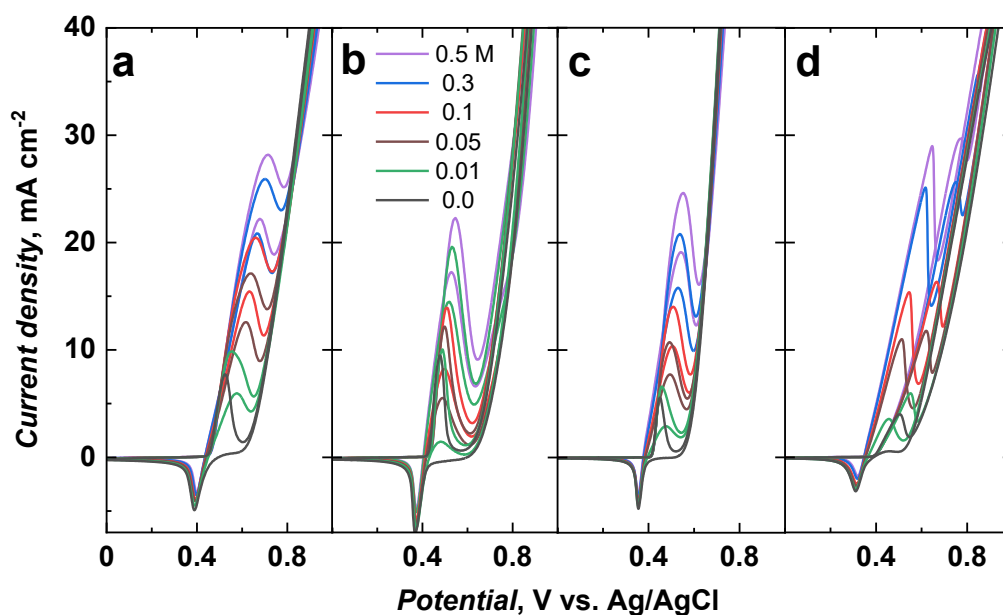


Figure 3.3-11. The catalytic CV responses of (a) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{0.2 M}, (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{0.5 M}, (c) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M}, and (d) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{2.0 M} catalysts toward the urea electrooxidation. The CVs were registered with the scan rate of 50 mV s⁻¹ in (a) 0.2 M NaOH_{aq}, (b) 0.5 M NaOH_{aq}, (c) 1.0 M NaOH_{aq}, and (d) 2.0 M NaOH_{aq}. Urea was continuously added to the electrochemical cell after each electrocatalysis step to achieve the desired concentration.

Ideally, the area under the oxidation peaks in both the forward and backward scans should be equal, indicating the active sites' high durability and availability after complete regeneration. This can be evaluated by calculating the charge associated with urea oxidation at the active centers, corresponding to the integrated area under the $I(t)$ curve. During the forward scan, the integrated area reflects the initial number of active sites (Q_1), while the area from the backward scan represents the active sites that remain accessible after the chemical oxidation (Q_2). By comparing these Q_1 and Q_2 values, the percentage of active poly(NPs-Ni³⁺OOHSalen) sites for catalysts derived under various NaOH_{aq} concentrations (Tables 3.3-2 – 3.3-5) can be determined.

Table 3.3-2. *In situ* active sites generation abilities of poly[NPs-Ni(OH)₂SaltMe]_{0.2 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{0.2 M} catalysts, determined under separate and continuous urea addition conditions.

	C_{urea} M	Poly[NPs-Ni(OH) ₂ SaltMe] _{0.2 M}			Poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe] _{0.2 M}		
		Q_1 mC cm ⁻²	Q_2 mC cm ⁻²	%Q	Q_1 mC cm ⁻²	Q_2 mC cm ⁻²	%Q
Separate	0.01	10.05	5.36	53.30	28.27	17.70	62.64
	0.05	22.09	12.24	55.43	63.27	47.55	75.16
	0.1	29.95	15.77	52.64	88.52	67.24	75.97
	0.3	43.37	21.02	48.47	108.06	91.48	84.66
	0.5	44.03	21.17	48.09	126.84	87.70	69.15
Continuous	0.01	11.28	5.05	44.80	27.14	11.73	43.23
	0.05	22.40	11.53	51.48	61.02	38.01	62.29
	0.1	29.08	14.69	50.53	78.47	49.39	62.94
	0.3	43.01	20.71	48.16	109.08	76.22	69.88
	0.5	46.43	21.94	47.25	123.11	83.01	67.43

For the poly[NPs-Ni(OH)₂Salen]_{0.2 M} catalysts tested in 0.2 M NaOH_{aq}, higher *in situ* generation abilities were observed for the poly[*meso*-NPs-Ni(OH)₂SaldMe]_{0.2 M} catalyst (Table 3.3-2). The highest *in situ* generation abilities values for separate (%Qs) and continuous (%Qc) urea additions were 84.7% and 69.9%, respectively, for 0.3 M urea for the poly[*meso*-NPs-Ni(OH)₂SaldMe]_{0.2 M} catalyst (Table 3.3-2). The *in situ* generation efficiency was lower when urea was continuously added in the 0.2 M NaOH_{aq}.

Table 3.3-3. *In situ* active sites generation abilities of poly[NPs-Ni(OH)₂SaltMe]_{0.5 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{0.5 M} catalysts, determined under separate and continuous urea addition conditions.

	C_{urea} M	Poly[NPs-Ni(OH) ₂ SaltMe] _{0.5 M}			Poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe] _{0.5 M}		
		Q ₁ mC cm ⁻²	Q ₂ mC cm ⁻²	%Q	Q ₁ mC cm ⁻²	Q ₂ mC cm ⁻²	%Q
Separate	0.01	12.81	1.89	14.74	14.69	4.23	28.82
	0.05	18.16	9.13	50.28	24.69	15.56	63.02
	0.1	23.47	15.31	65.22	32.60	24.13	74.02
	0.3	39.29	33.27	84.68	51.79	42.76	82.56
	0.5	45.61	39.80	87.25	64.49	55.36	85.84
Continuous	0.01	12.91	1.84	14.23	13.52	2.60	19.25
	0.05	18.06	8.47	46.89	20.77	11.89	57.25
	0.1	22.60	14.23	62.98	28.06	19.69	70.18
	0.3	35.00	28.57	81.63	47.96	40.05	83.51
	0.5	43.57	37.50	86.07	58.16	50.36	86.58

For poly[NPs-Ni(OH)₂SaltMe]_{0.5 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{0.5 M} in 0.5 M NaOH_{aq}, the %Q values increased with the increase of urea concentrations for both separate and continuous additions (Table 3.3-3). The highest *in situ* generation abilities were in the range 85.8-87.3 % for 0.5 M urea, for both catalysts, whether urea was added separately or continuously (Table 3.3-3).

Table 3.3-4. *In situ* active sites generation abilities of poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts, determined under separate and continuous urea addition conditions.

	C_{urea} M	Poly[NPs-Ni(OH) ₂ SaltMe] _{1.0 M}			Poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe] _{1.0 M}		
		Q_1 mC cm ⁻²	Q_2 mC cm ⁻²	%Q	Q_1 mC cm ⁻²	Q_2 mC cm ⁻²	%Q
Separate	0.01	13.93	7.81	56.04	10.41	5.97	57.35
	0.05	28.52	22.40	78.53	22.86	18.32	80.13
	0.1	36.84	28.67	77.84	34.03	28.16	82.76
	0.3	55.61	44.64	80.28	59.90	50.26	83.90
	0.5	66.22	54.08	81.66	74.80	63.27	84.58
Continuous	0.01	9.74	4.08	41.88	13.52	2.60	19.25
	0.05	18.52	12.91	69.70	20.77	11.89	57.25
	0.1	25.56	18.47	72.26	28.06	19.69	70.18
	0.3	41.17	30.92	75.09	47.96	40.05	83.51
	0.5	51.99	41.02	78.90	58.16	50.36	86.58

In 1.0 M NaOH_{aq}, once again, higher *in situ* generation ability was observed for poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst (Table 3.3-4). For separate urea additions at concentrations above 0.3 M, the %Qs values ranged from 80.3% to 81.7% for poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and from 83.9% to 84.6% for poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M}, indicating that greater amount of poly(*meso*-NPs-Ni³⁺OOHSaldMe)_{1.0 M} active sites remained accessible in the backward scan compared to poly(NPs-Ni³⁺OOHSaltMe)_{1.0 M}. During continuous urea additions, the *in situ* generation values were more divergent. For urea concentrations above 0.3 M, the %Qc values ranged from 75.1% to 78.9% for poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and from 83.5% to 86.6% for poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst. Significantly lower %Qc values for poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} catalyst suggested that product accumulation occurs on the catalyst under these conditions. Moreover, the variation in *in situ* generation values between separate and continuous additions was smaller for the poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst. This indicated that urea electrooxidation products were

effectively desorbing from the poly(*meso*-NPs-Ni³⁺OOHSaldMe)_{1.0 M} active sites, indicating that this catalyst is more resistant to the presence of the catalytic reaction products.

Table 3.3-5. *In situ* active sites generation abilities of poly[NPs-Ni(OH)₂SaltMe]_{2.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{2.0 M} catalysts, determined under separate and continuous urea addition conditions.

	C_{urea} M	Poly[NPs-Ni(OH) ₂ SaltMe] _{2.0 M}			Poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe] _{2.0 M}		
		Q ₁ mC cm ⁻²	Q ₂ mC cm ⁻²	%Q	Q ₁ mC cm ⁻²	Q ₂ mC cm ⁻²	%Q
Separate	0.01	12.76	8.57	67.20	10.26	7.70	75.12
	0.05	35.05	36.07	102.91	28.21	28.98	102.71
	0.1	68.42	64.03	93.59	46.33	46.53	100.44
	0.3	148.47	135.46	91.24	111.79	105.77	94.61
	0.5	ND	ND	ND	171.12	130.36	76.18
Continuous	0.01	19.85	8.62	43.44	11.94	6.94	58.12
	0.05	73.78	39.49	53.53	29.34	25.20	85.91
	0.1	ND	ND	ND	47.24	38.93	82.40
	0.3	ND	ND	ND	92.96	77.81	83.70
	0.5	ND	ND	ND	113.52	98.52	86.79

Urea and OH⁻ ions exhibit similar affinities for Ni(OH)₂-type active sites, allowing them to diffuse to the active centers competitively.¹²⁷ For poly[NPs-Ni(OH)₂SaltMe]_{2.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{2.0 M} in 2.0 M NaOH_{aq}, the electrooxidation peak current during the forward scan was shifted toward more positive potentials (Fig. 3.3-8, 3.3-9, 3.3-10, and 3.3-11). This shift suggested partial blocking of the active sites by OH⁻ ions. The peak shift became more pronounced when urea was added continuously (Fig. 3.3-10 and 3.3-11), suggesting that accumulated reaction products gradually blocked the poly(NPs-Ni³⁺OOHSalen)_{2.0 M} active sites, presumably due to the too high OH⁻ ion concentration. Furthermore, according to the Pourbaix diagram,¹⁷⁷ Ni(OH)₂ may be chemically unstable in

such highly alkaline media (2.0 M NaOH_{aq}) and could convert into HNiO₂⁻ *via* the reaction 3.3-3:



For poly[NPs-Ni(OH)₂SaltMe]_{2.0 M} catalyst, the peak shift was so significant that it overlapped with the OER, making it impossible to determine the *in situ* generation ability under both separate and continuous urea addition conditions (Table 3.3-5).

The highest *in situ* generation abilities of active sites were observed for poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts (Table 3.3-4), indicating that 1.0 M NaOH_{aq} is the optimal concentration for catalysts preparation. Among these two, the poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst exhibited a higher %Q value, suggesting that this catalyst revealed a greater resistance to the presence of catalytic reaction products.

For further analysis, selecting an optimal urea concentration at which the catalytic process becomes the rate-limiting step is important. Urea and OH⁻ ions compete for access to the active sites.¹²⁷ When the urea concentration is too low to overcome the binding affinity competition, the urea diffusion to the active centers would be the slowest step. Conversely, the catalytic reaction becomes the slowest step at sufficiently high urea concentrations. Under diffusion-controlled conditions, the anodic peak current density increases linearly with rising urea concentration.¹⁰⁷ The electrocatalytic CV responses recorded for separate urea additions (Fig. 3.3-8 and 3.3-9) were analyzed from this perspective, focusing on the linearity ranges. An increase in the forward anodic peak current density was visible for all poly[NPs-Ni(OH)₂Salen] catalysts with urea additions up to 0.3 M. This indicates that, up to this concentration, the urea amount was still insufficient to outcompete OH⁻ ions for access to the poly(NPs-Ni³⁺OOHSalen) active sites, and the process remained under diffusion control.

However, at urea concentrations exceeding 0.3 M, linearity was lost, indicating that the urea concentration became sufficient to overcome this competition, and the slowest step was the catalytic process. Based on this analysis, a urea concentration of 0.3 M was selected for further experiments.

3.3.4 Optimization of NaOH_{aq} concentration for the operation conditions of poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts

The onset potential is the lowest potential at which the reaction products begin to appear.^{105,146} It is one of the key parameters used to evaluate catalyst performance. High catalytic activity toward urea electrooxidation in alkaline media is typically indicated by both an increase in the anodic peak current density during the forward scan and a shift of the onset potential toward more negative values.⁹⁹ Consistently, greater resistance to poisoning by electrooxidation products is reflected by a higher anodic peak current density in the backward scan.^{107,121} Moreover, increasing the NaOH_{aq} concentration can decrease the onset potential and enhance the anodic current, promoting the oxidation of intermediates and the desorption of final reaction products from the catalyst surface.¹²⁸ Based on these considerations, poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts were investigated in the absence (Fig. 3.3-14) and presence of 0.3 M (Fig. 3.3-15) urea, in varying NaOH_{aq} concentrations.

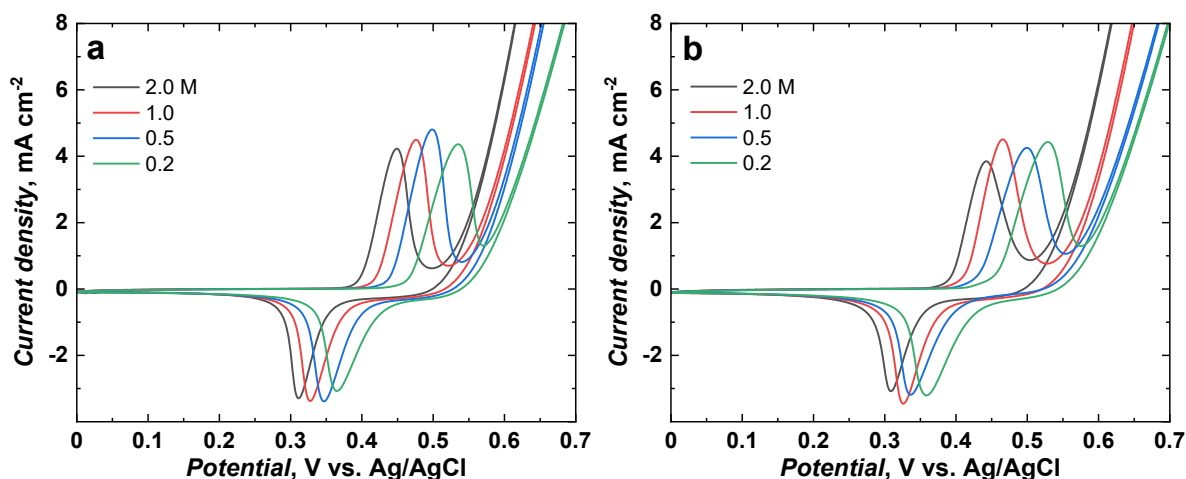


Figure 3.3-14. The CV responses of (a) poly[NPs-Ni(OH)₂SaltMe]_{1.0 M}, (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} in various NaOH_{aq} concentrations. The CVs were registered with a scan rate of 50 mV s⁻¹.

In the absence of urea (Fig. 3.3-14), the CV responses showed that with increasing NaOH_{aq} concentration, the poly[NPs-Ni²⁺(OH)₂Salen]_{1.0 M}/poly(NPs-Ni³⁺OOHSalen)_{1.0 M} oxidation/reduction peaks were shifted toward lower potentials. Higher current densities were observed for the poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst, indicating that a greater number of active sites were generated for this material. Among the tested NaOH_{aq} concentrations, the highest current densities were recorded for 0.5 and 1.0 M NaOH_{aq} (Fig. 3.3-14a, blue and red curves) for poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and 1.0 M NaOH_{aq} for poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} (Fig. 3.3-14b, red curves), suggesting that these concentrations were the most effective for active centers generation. In contrast, both poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts exhibited lower current densities in 2.0 M NaOH_{aq}, suggesting chemical instability and the occurrence of side reactions, an example is presented in Equation 3.3-3.

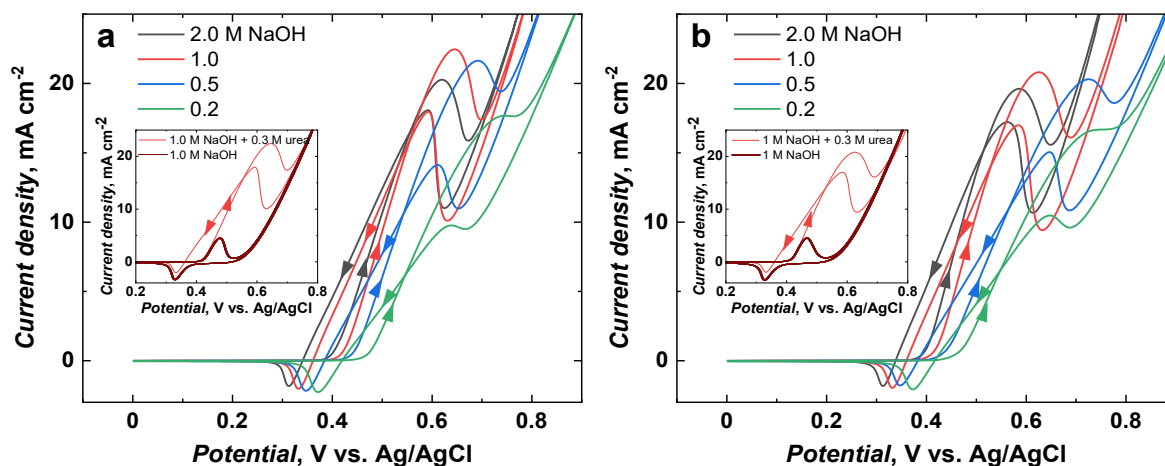


Figure 3.3-15. The catalytic CV responses of (a) poly[NPs-Ni(OH)₂SaltMe]_{1.0 M}, and (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} toward 0.3 M urea electrooxidation in 0.2, 0.5, 1.0, and 2.0 M NaOH_{aq}. Insets display comparison of CV responses both in the absence and presence of 0.3 M urea in 1.0 M NaOH_{aq} of (a) poly[NPs-Ni(OH)₂SaltMe]_{1.0 M}, and (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts. The CVs were recorded at a scan rate of 50 mV s⁻¹.

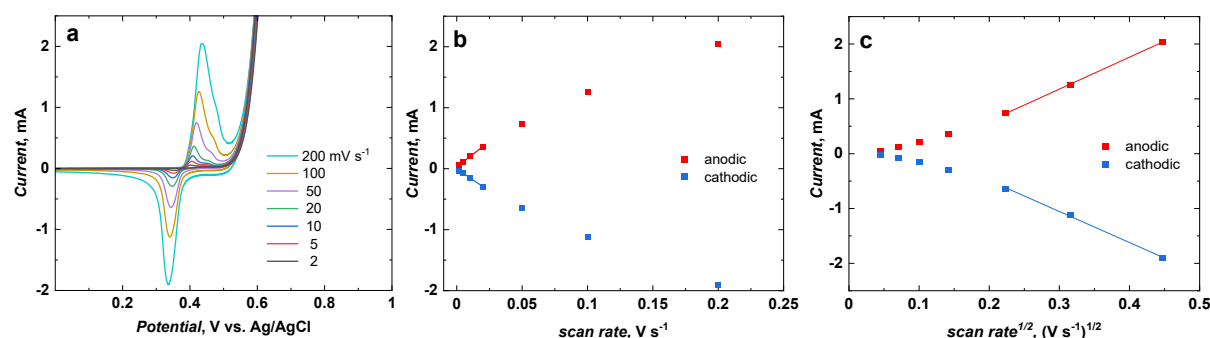
In 0.3 M urea (Fig. 3.3-15), both poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts exhibited a shift in the onset potential of urea electrocatalytic oxidation toward lower values with increasing NaOH_{aq} concentration. A lower onset potential (Table 3.3-6) was consistently observed for poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst for all NaOH_{aq} concentrations, indicating more effective generation of active sites for this catalyst and higher spatial accessibility of poly(*meso*-NPs-Ni³⁺OOHSaldMe)_{1.0 M} active sites to urea and OH⁻ ions. However, in 2.0 M NaOH_{aq} (Fig. 3.3-15, black curves), it looked like this accessibility was disrupted. This is reflected in the lack of a proportional increase in catalytic current density with decreasing onset potential, likely due to excessive OH⁻ adsorption. As a result, the urea electrooxidation peak merged with the OER.¹⁷⁸ These findings indicated that 1.0 M NaOH_{aq} is an optimal operating concentration for both poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts.

Table 3.3-6. Onset potential for the electrooxidation of 0.3 M urea in 0.2, 0.5, 1.0, and 2.0 M for the poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts.

C_{NaOH} (M)	Poly[NPs-Ni(OH) ₂ SaltMe] _{1.0 M} Onset potential (V)	Poly[<i>meso</i> -NPs-Ni(OH) ₂ SaldMe] _{1.0 M} Onset potential (V)
0.2	0.474	0.466
0.5	0.445	0.438
1.0	0.424	0.416
2.0	0.406	0.399

3.3.5 Electrochemical characterization of poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts

The multiple scan rate experiment was carried out in the absence of the urea for two catalysts: poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} (Fig. 3.3-16 and 3.3-18) and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} (Fig. 3.3-17 and 3.3-19). These catalysts, derived in 1.0 M NaOH_{aq}, exhibited the best electrocatalytic performance toward urea electrooxidation (Fig. 3.3-8 and 3.3-9). The purpose of this experiment was to determine the limiting conditions of the poly[NPs-Ni²⁺(OH)₂Salen]_{1.0 M}/poly(NPs-Ni³⁺OOHSalen)_{1.0 M} oxidation/reduction redox process influenced by the electrochemical dopant concentration for both differently structured materials. CV responses were registered at scan rates of 2, 5, 10, 20, 50, 100, and 200 mV s⁻¹ in the 1.0 and 2.0 M NaOH_{aq}.



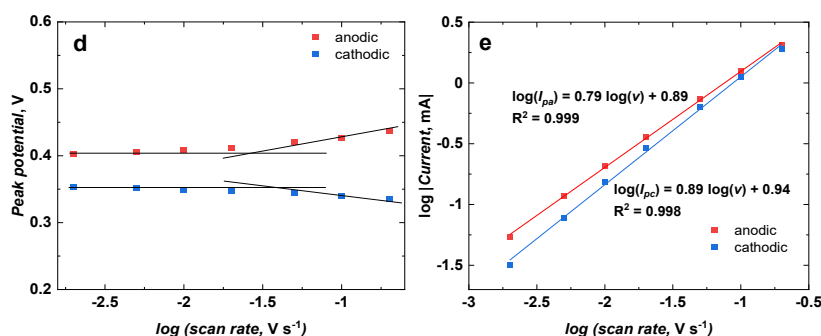


Figure 3.3-16. (a) CV curves of poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} performed at different scan rates in 1.0 M NaOH_{aq}. (b) The anodic (red curve) and cathodic (blue curve) peak current vs. the scan rate. (c) The anodic (red curve) and cathodic (blue curve) peak current vs. the square root of the scan rate (d) The anodic (red curve) and cathodic (blue curve) peak potential vs. the logarithm of the scan rate (e) The logarithm of the anodic (red curve) and cathodic (blue curve) peak current dependence on the logarithm of the scan rate.

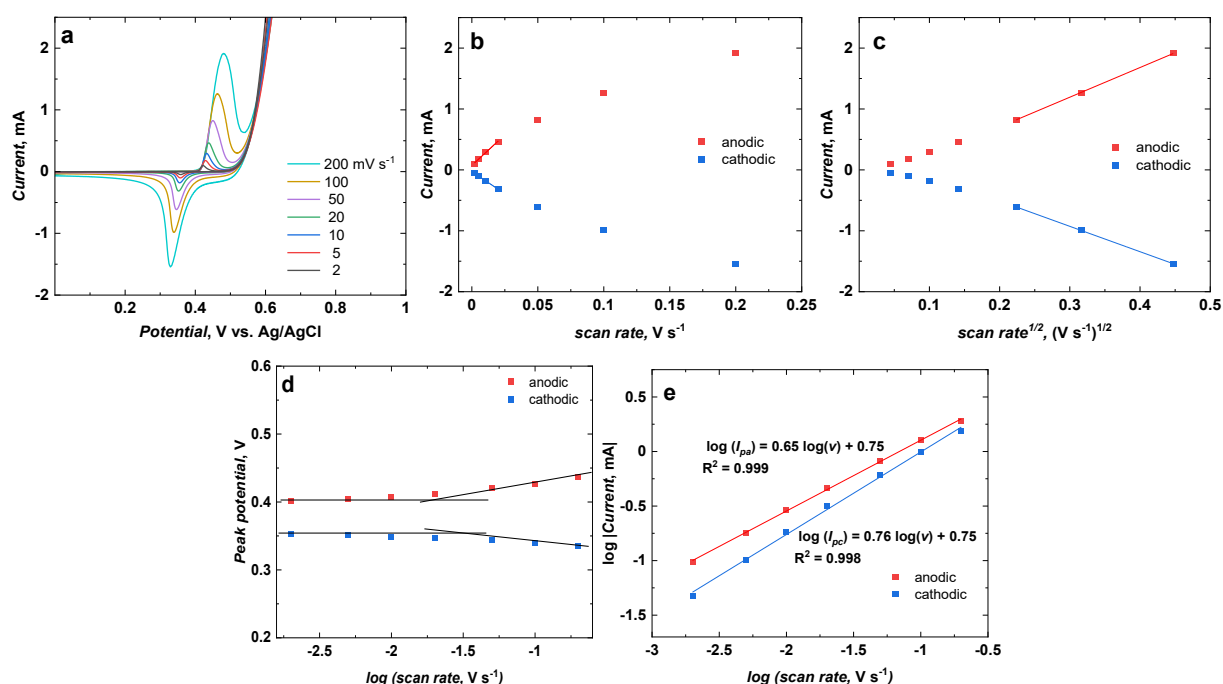


Figure 3.3-17. (a) CV curves of poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} performed at different scan rates in 1.0 M NaOH_{aq}. (b) The anodic (red curve) and cathodic (blue curve) peak current vs. the scan rate. (c) The anodic (red curve) and cathodic (blue curve) peak current vs. the square root of the scan rate (d) The anodic (red curve) and cathodic (blue curve) peak potential vs. the logarithm of the scan rate (e) The logarithm of the anodic (red curve) and cathodic (blue curve) peak current dependence on the logarithm of the scan rate.

The CV curves recorded at various scan rates in 1.0 and 2.0 M NaOH_{aq} for poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} (Fig. 3.3-16a and 3.3-18a) and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} (Fig. 3.3-17a and 3.3-19a) exhibited one oxidation/reduction peak corresponding to the poly[NPs-Ni²⁺(OH)₂Salen]_{1.0 M}/poly(NPs-Ni³⁺OOHSalen)_{1.0 M} redox couple. These peak currents showed a linear dependence on scan rate up to 20 mV s⁻¹ (Fig. 3.3-16b, 3.3-17b, 3.3-18b, and 3.3-19b), indicating that the redox process was under finite-diffusion control¹⁴² within this scan rate range. At scan rates above 20 mV s⁻¹, in both 1.0 M (Fig. 3.3-16c and 3.3-17c) and 2.0 M NaOH_{aq} (Fig. 3.3-18c and 3.3-19c), the peak currents began to exhibit a linear dependence on the square root of the scan rate, suggesting that the diffusion of OH⁻ ions was close to entering the semi-infinite diffusion regime.¹⁴⁰

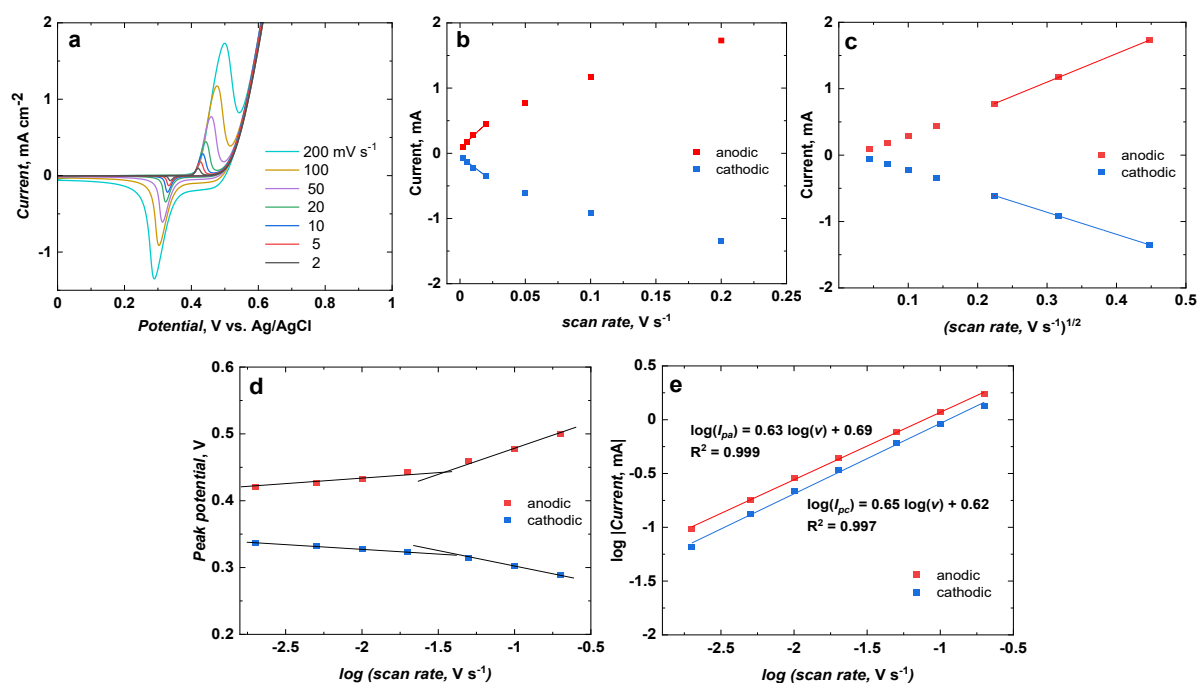


Figure 3.3-18. (a) CV curves of poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} performed at different scan rates in 2.0 M NaOH_{aq}. (b) The anodic (red curve) and cathodic (blue curve) peak current vs. the scan rate. (c) The anodic (red curve) and cathodic (blue curve) peak current vs. the square root of the scan rate (d) The anodic (red curve) and cathodic (blue curve) peak potential vs. the logarithm of the scan rate (e) The logarithm of the anodic (red curve) and cathodic (blue curve) peak current dependence on the logarithm of the scan rate.

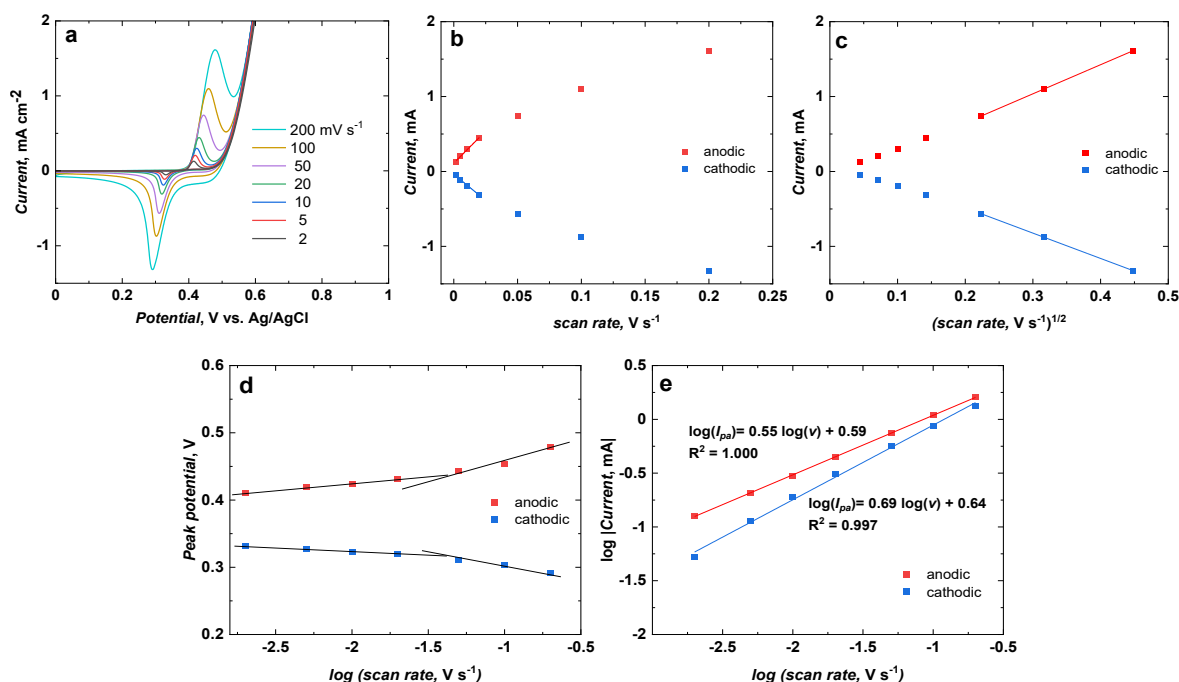


Figure 3.3-19. (a) CV curves of poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} performed at different scan rates in 2.0 M NaOH_{aq}. (b) The anodic (red curve) and cathodic (blue curve) peak current vs. the scan rate. (c) The anodic (red curve) and cathodic (blue curve) peak current vs. the square root of the scan rate (d) The anodic (red curve) and cathodic (blue curve) peak potential vs. the logarithm of the scan rate (e) The logarithm of the anodic (red curve) and cathodic (blue curve) peak current dependence on the logarithm of the scan rate.

Among the multiple scan rate responses registered in 1.0 and 2.0 M NaOH_{aq} for both materials, a higher current value, coupled with the Nernstian electrochemical behavior, was observed for the catalysts operating in 1.0 M NaOH_{aq}. Accordingly, the peak potential separation remained low at scan rates up to 20 mV s⁻¹ for both catalysts in 1.0 M NaOH_{aq} (Fig. 3.3-16d and 3.3-17d), but increased at higher scan rates due to the inability of OH⁻ ions diffusion to keep the charge transfer rate. For both catalysts in 2.0 M NaOH_{aq}, lower current values (Fig. 3.3-18a and 3.3-19a), higher peak potential separations (Fig. 3.3-18d and 3.3-19d), and lower values of slopes of the log(*I*) vs. log(*v*) plots (Fig. 3.3-18e and 3.3-19e) were observed compared to those in 1.0 M NaOH_{aq}. Those findings indicated hindered OH⁻ ions diffusion to the active sites,

suggesting that in 2.0 M NaOH_{aq} poly(NPs-Ni³⁺OOHSaltMe)_{1.0 M} and poly(*meso*-NPs-Ni³⁺OOHSaldMe)_{1.0 M} active sites may be blocked by too strong adsorption of OH⁻ counterions, potentially leading to chemical degradation of these centers.

The differences in the multiple scan rate responses recorded for both catalysts in 1.0 M NaOH_{aq} indicated that the poly[NPs-Ni²⁺(OH)₂Salen]_{1.0 M} $\rightleftharpoons$ poly(NPs-Ni³⁺OOHSalen)_{1.0 M} electrochemical redox process is governed by OH⁻ finite diffusion control. The slope value of the log(*I*) vs. log(*v*) dependence for poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} (Fig. 3.3-16e) was 0.79, which corresponds to the surface process.¹⁴⁴ For poly(*meso*-NPs-Ni(OH)₂SaldMe)_{1.0 M} (Fig. 3.3-17e), this slope was 0.65, indicating that the fast electrochemical process occurred in the bulk of the catalyst. This indicates that the poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} catalyst possesses a relatively flat structure with active sites located near the surface. In contrast, the poly(*meso*-NPs-Ni(OH)₂SaldMe)_{1.0 M} catalyst exhibits a more spatially diversified structure, with active sites embedded in the bulk of the matrix.

3.3.6 Urea electrooxidation on the poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly(*meso*-NPs-Ni(OH)₂SaldMe)_{1.0 M} catalysts

In the next step, multiple scan rate responses were recorded for the poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} (Fig. 3.3-20) and poly(*meso*-NPs-Ni(OH)₂SaldMe)_{1.0 M} (Fig. 3.3-21) catalysts in 1.0 M NaOH_{aq} containing 0.3 M urea, to evaluate which catalyst exhibits better catalytic performance. To determine differences in the electrocatalytic urea oxidation at both catalysts, the results obtained for pure 1.0 M NaOH_{aq} (reflecting active sites generation) were compared with those obtained in the presence of urea (reflecting active sites accessibility).

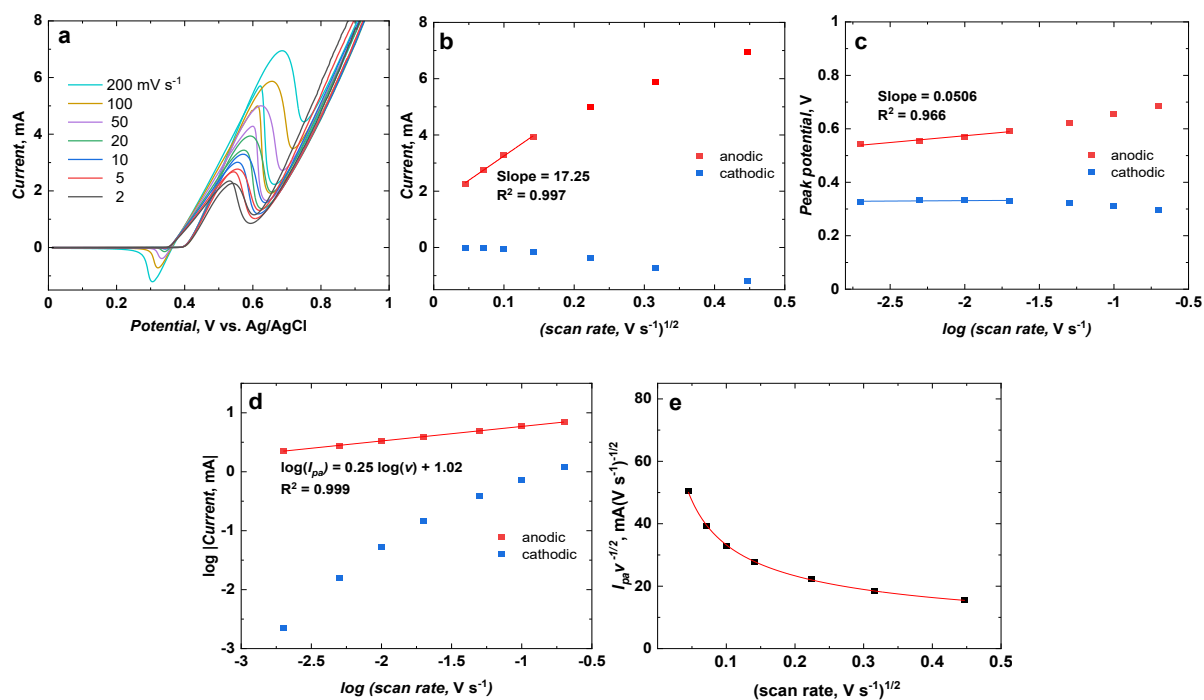


Figure 3.3-20. (a) CV curves of poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} performed at different scan rates in the presence of 0.3 M urea in 1.0 M NaOH_{aq}. (b) The anodic and cathodic peak currents vs. the square root of the scan rate. (c) The anodic and cathodic peak potentials vs. the logarithm of the scan rate. (d) The logarithm of the anodic and cathodic peak currents vs. the logarithm of the scan rate. (e) The scan rate normalized current ($I_{pa} v^{-1/2}$) vs. the square root of the scan rate.

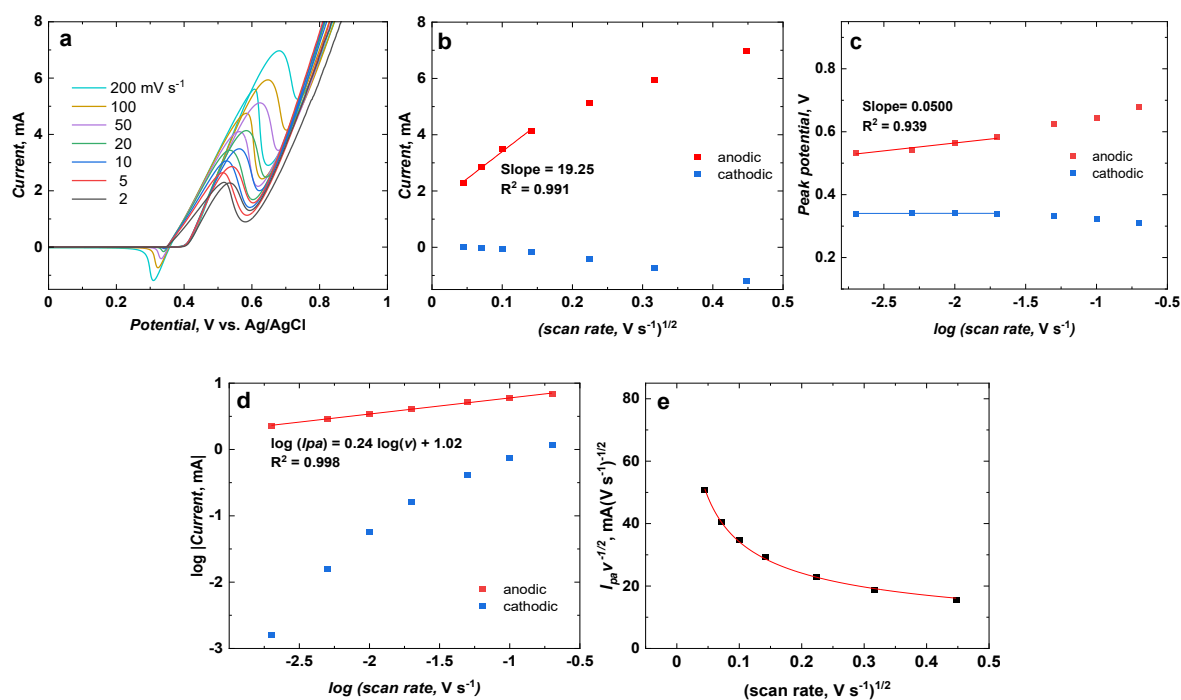
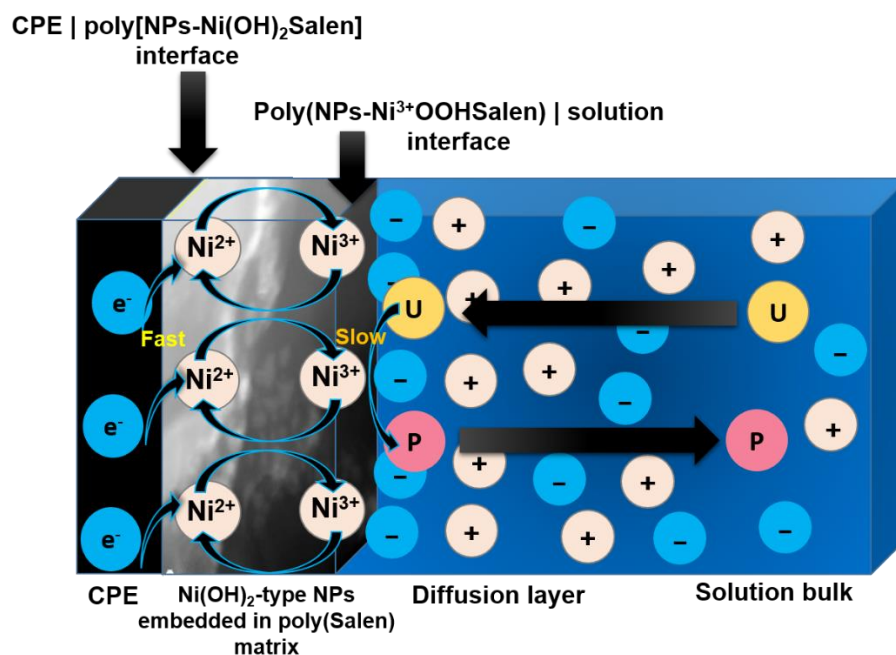


Figure 3.3-21. (a) CV curves of poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} performed at different scan rates in the presence of 0.3 M urea in 1.0 M NaOH_{aq}. (b) The anodic and cathodic peak currents vs. the square root of the scan rate. (c) The anodic and cathodic peak potentials vs. the logarithm of the scan rate. (d) The logarithm of the anodic and cathodic peak currents vs. the logarithm of the scan rate. (e) The scan rate normalized current ($I_{pa} v^{-1/2}$) vs. the square root of the scan rate.

The electrocatalytic responses toward the electrooxidation of 0.3 M urea in 1.0 M NaOH_{aq} for both catalysts showed an increase in peak current with increasing scan rate (Fig. 3.3-20a and 3.3-21a). For scan rates below 20 mV s⁻¹, the peak current was linearly dependent on the square root of the scan rate, indicating that the process was under charge-transfer control. At scan rates above 20 mV s⁻¹, the generation of active sites becomes slower, and the electrochemical process is controlled by OH⁻ diffusion, as confirmed by the experiments carried out in pure 1.0 M NaOH_{aq} (Fig. 3.3-16 and 3.3-17). Moreover, the dependence of the catalytic peak currents, normalized with the square root of the scan rate, versus the scan rate (Fig. 3.3-20e and 3.3-21e) showed a rapid drop in normalized current up to 20 mV s⁻¹, confirming that, under these conditions, the chemical oxidation of urea was the controlling step. At scan rates above 20 mV s⁻¹, the normalized current remained relatively constant, indicating that the generation of active centers was slower because of the OH⁻ diffusion limitations. Additionally, the slope of the log(*I*) vs. log(*v*) plot in the 2 – 20 mV s⁻¹ scan rate range was 0.25 for poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} catalyst (Fig. 3.3-20d) and 0.24 for poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst (Fig. 3.3-21d), indicating that the Ni³⁺OOH active sites embedded in the poly(*meso*-SaldMe) matrix were more accessible to urea.



Scheme 3.3-1. Illustration showing the two-step urea electrocatalytic oxidation at poly[NPs-Ni(OH)₂Salen] (CPE – Carbon paper electrode; P – Product; U – Urea).

In the next step, based on data from multiple scan rate experiments, α and D values were calculated to quantify differences in molecular structure between the catalysts and their implications for the urea electrooxidation process. The α is related to the electrocatalytic charge transfer occurring at the 2nd interface of poly(NPs-NiOOHSalen) | urea (Scheme 3.3-1) and falls within the range of 0 to 1. Values below 0.5 indicate a one-electron transfer process, while values above 0.5 indicate a multi-step process. α value was determined from the linear dependence of E vs. $\log(\nu)$ in the scan rate range of 2 to 20 mV s⁻¹, according to Equation 3.3-4.

$$\alpha = \frac{0.03}{\text{slope } n_0} \quad (3.3-4)$$

The calculated α was 0.59 for poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} catalyst and 0.60 for poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst. These results confirm that urea is electrooxidized *via* a two-

step indirect mechanism, in which six electrons are exchanged during the charge transfer at the 2nd interface (Scheme 3.3-1).

The diffusion coefficient (D) describes how quickly urea molecules can reach the poly(NPs-NiOOHSalen) active sites.¹⁰⁷ The D value was calculated from the linear dependence of I vs. $\log(\nu)$ in the scan rate range of 2 to 20 mV s⁻¹, using Equation 2.3-6. The calculated D was 5.87×10^{-7} cm² s⁻¹ for poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} catalyst and 7.49×10^{-7} cm² s⁻¹ for poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst. The higher D value means that urea molecules can more rapidly diffuse to the poly(*meso*-NPs-Ni³⁺OOHSaldMe) active sites, indicating that poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst possesses a more spatially diversified molecular structure, which facilitates the electrocatalytic process.

3.3.7 Electrochemical characterization of the urea electrooxidation process on the poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts

In the next step, CV responses were registered in various temperatures (16, 19, 24, 28, 33, 38, and 43 °C) in 1.0 M NaOH_{aq}, both in the absence and presence of 0.3 M urea, to study the influence of temperature on the overall two-step electrocatalytic process and to determine the E_{ac} of urea electrooxidation for the poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts. The E_{ac} values were determined at 0.45 and 0.50 V (potentials corresponding to the urea electrooxidation) based on Arrhenius plots ($\log(I)$ vs. $1/T$).

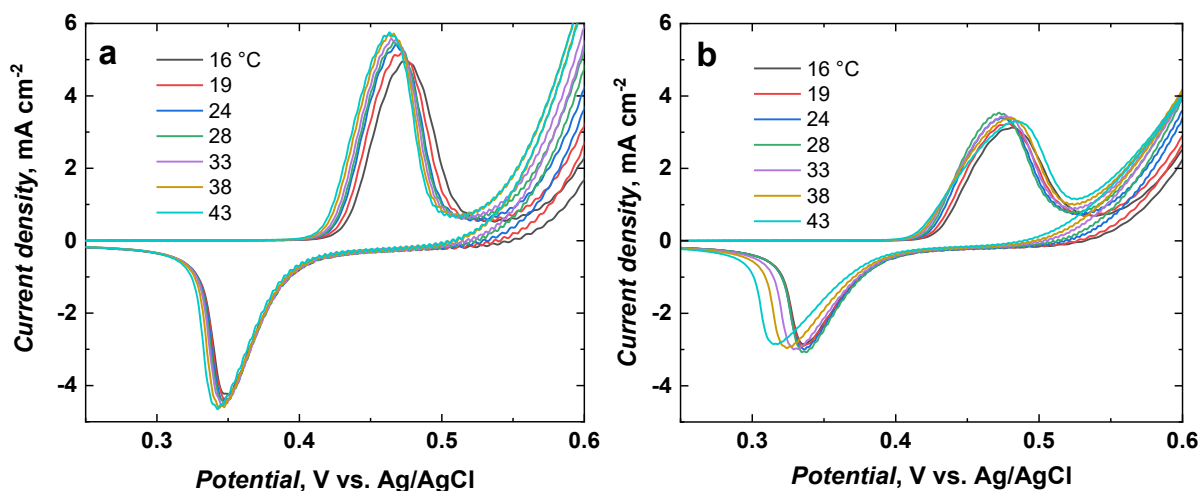


Figure 3.3-22. CV responses measured in 1.0 M NaOH_{aq} at various temperatures for electrocatalyst (a) poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} at a scan rate of 50 mV s⁻¹.

The CV responses registered without urea for the poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} catalyst showed that increasing temperature led to a slight increase in current density, accompanied by a shift of the peak potential toward lower values (Fig. 3.3-22). This indicated that the poly(NPs-Ni³⁺OOHSaltMe)_{1.0 M} active sites were generated more efficiently at higher temperatures. A similar trend was observed for the poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst at temperatures below 28 °C (Fig. 3.3-22). However, further increases in temperature led to a decrease in peak current density and a shift in the peak potential toward more positive values, suggesting hindered dedoping of OH⁻ from the poly(*meso*-NPs-Ni³⁺OOHSaldMe)_{1.0 M} active sites. This behavior is connected with a more spatially diversified structure of the poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst, in which active sites are embedded within the bulk of the poly(*meso*-SaldMe)_{1.0 M} matrix.

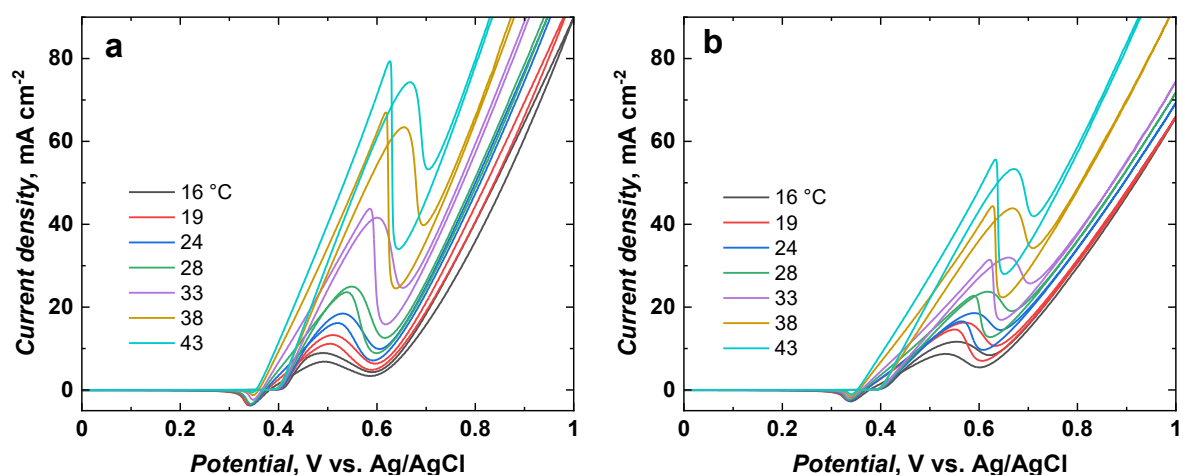


Figure 3.3-23. (a) poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} electrocatalytic CV responses measured at different temperatures in the solution containing 0.3 M urea in 1.0 M NaOH_{aq}.

In the presence of 0.3 M urea (Fig. 3.3-23), an increase in temperature resulted in a higher peak current density and onset peak potential shift toward lower values, indicating that electrocatalytic urea oxidation became more favorable at elevated temperatures. Additionally, a shift in the urea electrooxidation peak was observed with increasing temperature, but its interpretation differs between the two catalysts and relates to the behavior observed in pure 1.0 M NaOH_{aq} (Fig. 3.3-22). For the poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} catalyst, the shift indicated accumulation of urea electrooxidation products, as this catalyst did not exhibit hindered OH⁻ desorption in the control experiment (Figure 3.3-22). In contrast, the poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst showed clear hindered OH⁻ desorption, both in the absence and presence of urea. Additionally, observed hindered OH⁻ dedoping from the spatially diversified poly(*meso*-NPs-NiOOHSaldMe)_{1.0 M} active sites facilitated the final desorption of urea electrooxidation products. These observations further supported conclusions from the *in situ* generation ability of active sites.

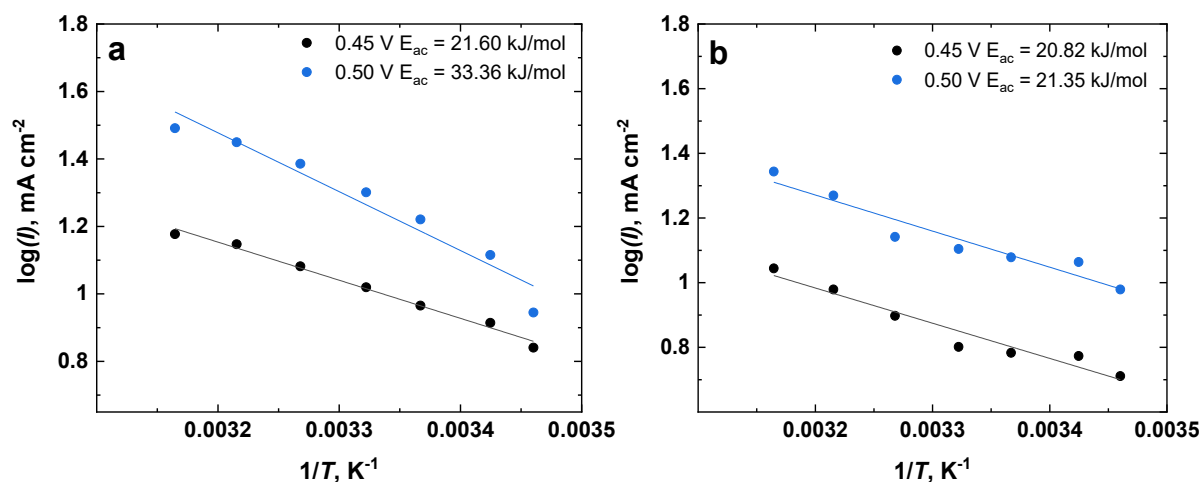


Figure 3.3-24. Arrhenius plots made for (a) poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} electrocatalysts based on the data from Figure 3.3-23.

Arrhenius plots [$\log(I)$ vs. $1/T$] were constructed for 0.45 and 0.50 V, potentials corresponding to the urea electrooxidation process on the poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts (Fig. 3.3-24). The obtained linear relationships confirmed that the two-step indirect mechanism of urea electrooxidation remained unchanged across all studied temperatures.¹⁷⁹ The E_{ac} values were calculated from Equation 2.3-9. The lower E_{ac} values determined for the poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst (20.82 kJ mol⁻¹ for 0.45 V and 21.35 kJ mol⁻¹ for 0.50 V) compared to the poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} catalyst (21.60 kJ mol⁻¹ for 0.45 V and 33.36 kJ mol⁻¹ for 0.50 V) indicated that the poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst exhibited higher catalytic activity toward urea electrooxidation.

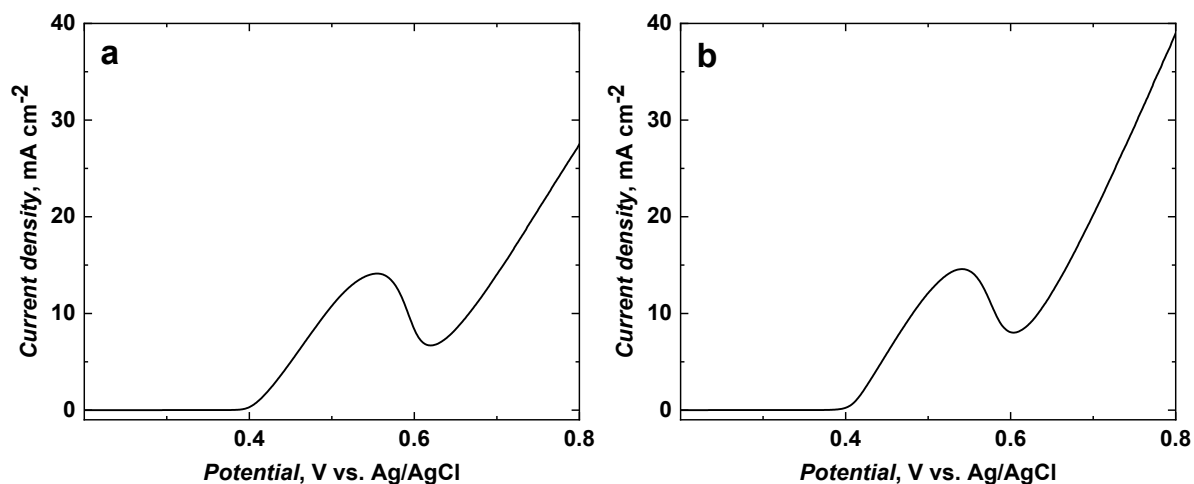


Figure 3.3-25. LSV curves measured for electrocatalysts (a) poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} registered at 5 mV s⁻¹ in the solution containing 0.3 M urea in 1.0 M NaOH_{aq}.

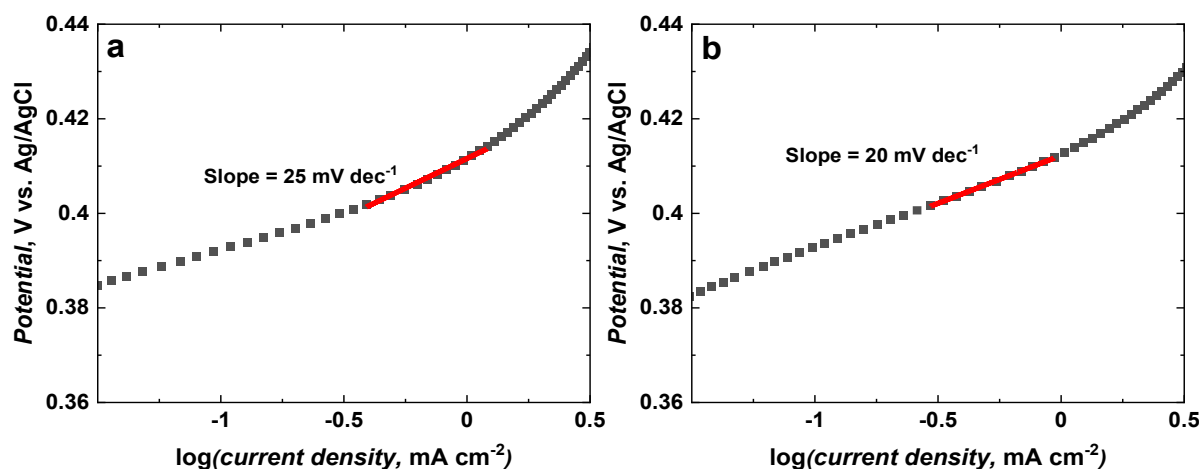


Figure 3.3-26. Tafel slopes determined for (a) poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M}, electrocatalysts in the presence of 0.3 M urea in 1 M NaOH_{aq}.

The Tafel slope was determined to evaluate which catalyst generates catalytic current more efficiently in response to changes in applied potential. Tafel slope was derived from LSV curves (Fig. 3.3-25) measured at a scan rate of 5 mV s⁻¹ over the potential range of 0 to 1.0 V vs. Ag/AgCl (3 M KCl) in a 1.0 M NaOH_{aq} solution containing 0.3 M urea. These conditions

ensured that the electrooxidation of urea at the accessible active centers was the slowest step.¹⁴⁰ The Tafel slope was obtained from the E vs. $\log(I)$ dependence (Fig. 3.3-26). The calculated Tafel slopes were 25 mV dec^{-1} for poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} catalyst and 20 mV dec^{-1} for poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst. This indicates that the poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst exhibits a significant current density increment as a function of the overpotential change and thus produces catalytic current more efficiently in response to a change in the applied potential. Moreover, the obtained Tafel slopes are lower than those reported for many other urea electrocatalysts, highlighting the superior performance of these materials.^{93,124}

3.3.8 Durability test of poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts in real sample mimicking conditions

Constant-potential experiments were conducted to simulate the operating conditions of the anode in UFC. Chronoamperometric experiments were conducted by applying a constant potential of $0.55 \text{ V vs. Ag/AgCl (3 M KCl)}$ for 17 hours in $1.0 \text{ M NaOH}_{\text{aq}}$, both in the absence and presence of 0.3 M urea and artificial urine, using poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts. The applied 0.55 V potential ensured electrocatalytic oxidation of urea in a real-system mimicking conditions.

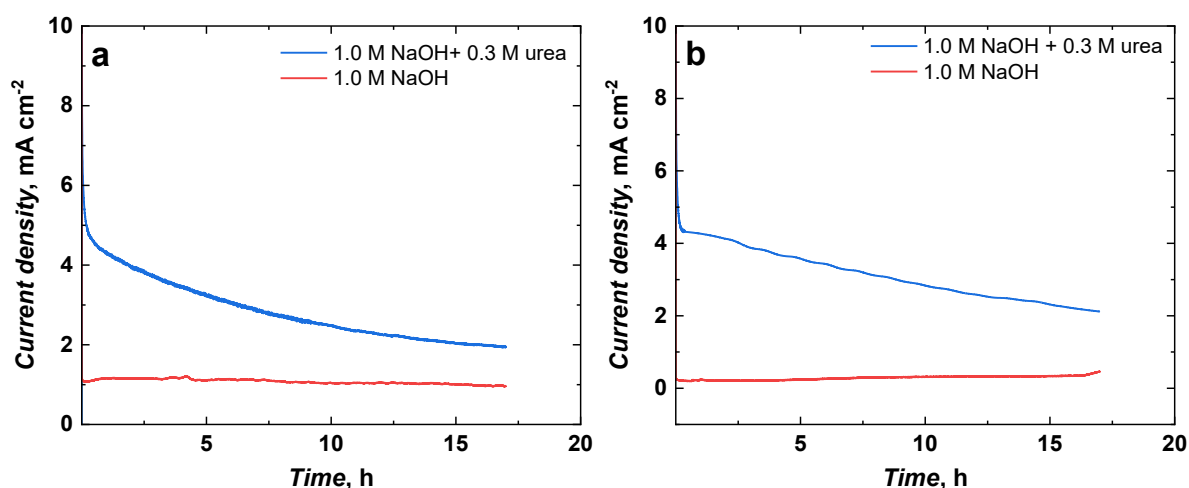


Figure 3.3-27. Chronoamperometric measurements conducted in the absence and presence of urea for electrocatalysts (a) poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and (b) poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} at a constant potential of 0.55 V vs. Ag/AgCl.

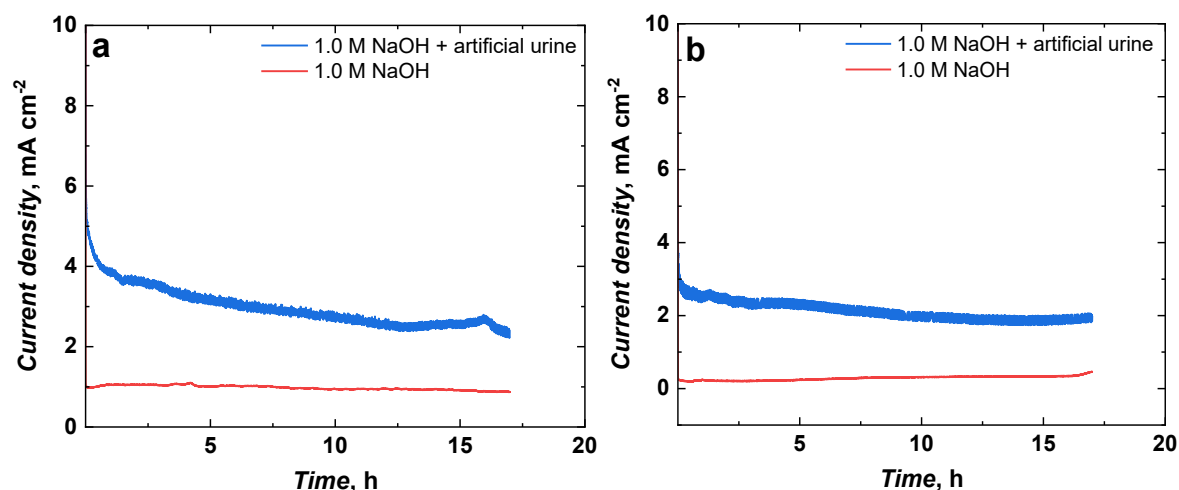


Figure 3.3-28. Chronoamperometric measurements conducted in the absence and presence of urea in the real system mimicking solution for (a) poly[NPs-Ni(OH)₂SaltMe]_{1 M} and (b) poly[*meso*-NPs Ni(OH)₂SaldMe]_{1 M} electrocatalysts at a constant potential of 0.55 V vs. Ag/AgCl.

Control experiments performed in the absence of urea and in real sample mimicking solution¹³¹ (containing 0.25 M urea) showed a stable current density over time, indicating that the amount of catalytically active poly(NPs-Ni³⁺OOHSaltMe)_{1.0 M} and poly(*meso*-NPs-Ni³⁺OOHSaldMe)_{1.0 M} sites remained constant during the 0.55 V potential application (Fig. 3.3-27 and 3.3-28, red curves). In contrast, chronoamperometric measurements in the presence of urea (Fig. 3.3-27, blue curves) revealed a gradual decrease in current density, suggesting a reduction in the number of accessible poly(NPs-Ni³⁺OOHSalen)_{1.0 M} active centers. This observation supports the proposed indirect mechanism of urea electrooxidation, in which poly(NPs-Ni³⁺OOHSalen)_{1.0 M} active sites are reduced to poly[NPs-Ni²⁺(OH)₂Salen]_{1.0 M} during the catalytic process. After 15 hours, current retention was 44%

for poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} catalyst and 56% for poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalyst. Notably, current retention values for artificial urine sample (Fig. 3.3-28, blue curves) were higher than those observed in pure urea solution, and were 65% for poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and 70% for poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M} catalysts. This improvement can be attributed to the higher conductivity of the artificial urine solution in 1.0 M NaOH_{aq}, which enhanced the efficiency of the electrocatalytic process compared to the pure urea solution.¹⁸⁰

These long-term stability tests in real system mimicking conditions confirmed that both catalysts, poly[NPs-Ni(OH)₂SaltMe]_{1.0 M} and poly[*meso*-NPs-Ni(OH)₂SaldMe]_{1.0 M}, are promising materials for the remediation of urea-rich wastewater.

4 Conclusions and future prospects

This dissertation presented a comprehensive strategy for the structural tuning of poly[NPs-Ni(OH)₂Salen] based electrocatalyst for efficient ethanol and urea electrooxidation. The catalytic performance of the electrogenerated poly[NPs-Ni(OH)₂Salen] catalysts was found to be strongly governed by the chemical structure of the NiSalen complexes and the morphology of deposited poly(NiSalen) precursors.

Appropriate selection of NiSalen monomer structure combined with its controlled deposition conditions enables adapted changes of polymer morphology and consequently the distribution and accessibility of Ni³⁺OOH active sites embedded in the polymer matrix. Poly(NiSalen) precursors were deposited on the CP electrode under PS and PD conditions, with comparable deposition charge, leading to the formation of precursors with distinct morphologies. All precursors underwent potential-driven transformation in alkaline media into Ni(OH)₂-based NPs, embedded in a polymer matrix. The number of potential cycles required for the complete generation of Ni(OH)₂ type NPs depended on the electrochemical stability of the precursor in the moderately ED organic solvent. The mechanism of this potential-driven transformation was elucidated, revealing a change of the primary target of electron release from the Salen ligand center to the Ni center in NaOH_{aq}.

The chemical structure of the unsubstituted complex was further tuned by introducing an ED methoxy substituent at the 3-position of both salicylaldehyde moieties. This resulted in a less uniform, more structurally developed poly(NiSalen-3dOMe) precursors leading to a more spatially developed structure in the derived catalysts. This significantly enhanced the electrocatalytic activity of poly[NPs-Ni(OH)₂SaldMe-3dOMe] and poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe] catalysts for ethanol electrooxidation in comparison to unsubstituted ones. Obtained catalytic current densities for 0.3 M ethanol in 0.1 M NaOH were 29.6 and

35.5 mA cm⁻² for poly[*meso*-NPs-Ni(OH)₂SaldMe]-PS_{low}, and poly[*meso*-NPs-Ni(OH)₂SaldMe-3dOMe]-PS, respectively, indicating better catalytic performance of substituted catalysts.

Morphology studies further establish a correlation between precursor morphology and electrocatalytic performance. It revealed that relatively flat poly(NiSaltMe) promoted 2D organization of Ni(OH)₂ NPs in matrices, whereas a globular poly(*meso*-NiSaldMe) and poly(*meso*-NiSaldMe-3dOMe) precursors arranged Ni(OH)₂ NPs in spatially diversified 3D matrices, which provided improved accessibility of active sites and resulted in higher electrocatalytic current densities.

Poly[NPs-Ni(OH)₂Salen] catalysts demonstrated resistance to ethanol electrooxidation products, and no catalyst poisoning was observed. In contrast, the application of these electrocatalysts in urea electrooxidation appeared more challenging due to the stronger adsorption of reaction intermediates on active sites. Therefore, a comprehensive optimization of catalyst generation and operation conditions was performed. Combined SEM/TEM analysis and evaluation of the *in situ* active sites generation abilities, based on an indirect mechanism, enabled the identification of the best catalyst fabrication as well as operation conditions. Both catalysts showed the highest activity in 1.0 M NaOH_{aq} containing 0.3 M urea. Moreover, the obtained results revealed a structure-activity relationship between poly[NPs-Ni(OH)₂SaltMe] and poly[*meso*-NPs-Ni(OH)₂SaldMe] catalysts. In poly[NPs-Ni(OH)₂SaltMe], the active sites were mainly located on the catalyst surface, whereas in poly[*meso*-NPs-Ni(OH)₂SaldMe], they were distributed throughout the catalyst bulk. The more uniform spatial distribution of poly(*meso*-NPs-Ni³⁺OOHSaldMe) active sites resulted in improved stability during urea electrooxidation.

Finally, measurements conducted under real system mimicking conditions confirmed the applicability of the developed poly[NPs-Ni(OH)₂Salen] catalysts for the remediation of urea-rich wastewater. Hence, the current retention values after 15 h of electrooxidation were ~65% and ~70% for the poly[NPs-Ni(OH)₂SaltMe] and poly[*meso*-NPs-Ni(OH)₂SaldMe] catalysts, respectively. This demonstrated their potential for simultaneous wastewater treatment and energy generation. 3D distribution of poly(*meso*-NPs-NiOOHSaldMe)_{1 M} catalytically active sites provided better sustainability during urea electrooxidation in a real system mimicking solution. Moreover, the Tafel slope of 20 mV dec⁻¹ and E_a of 20.82 kJ mol⁻¹ confirmed that this 3D structured catalyst is highly active towards UOR.

The results presented in this thesis open new directions for the further development of poly[NPs-Ni(OH)₂Salen] electrocatalysts. The ability to tailor catalytic performance through the complexes chemical structure, electrodeposition conditions, and the optimization of the potential-driven transformation provides a useful approach for designing catalysts with improved activity and stability. Future research may focus on introducing various ED substituents to tune the distribution of active sites in non-conductive matrices.

A promising direction for future research is to explore the roles of different metal centers within the salen-based framework. The presented thesis was focused on Ni(OH)₂ NPs-based systems. Replacing Ni with other transition metals, such as cobalt, copper, or iron, can significantly influence the redox catalytic performance of the resulting materials. Different metals may improve selectivity or activity toward specific electrochemical reactions. Therefore, systematic studies on metal substitution may provide further insight into structure-activity relationships and enable the development of more efficient and versatile electrocatalytic systems.

To address these research directions, a set of new monomers incorporating various substituents and cobalt as the central metal has already been synthesized. These compounds will enable a

systematic evaluation of the effects of ligand structure and the metal center on the potential-driven transformation process and the catalytic behavior of the resulting catalysts. The synthesized monomers are as follows:

- 2,3-dimethyl-*N, N'*-bis(salicylidene)-2,3-butanediaminocobalt (CoSaltMe)
- 2,3-dimethyl-*N, N'*-bis(3-methylsalicylidene)-2,3-butanediaminonickel (CoSaltMe-3dMe),
- 2,3-dimethyl-*N, N'*-bis(3-methoxysalicylidene)-2,3-butanediaminocobalt (CoSaltMe-3dOMe),
- 2,3-dimethyl-*N, N'*-bis(3-ethoxysalicylidene)-2,3-butanediaminonickel (NiSaltMe-3dOEt),
- *meso*-*N, N'*-bis(3-ethoxysalicylidene)-2,3-butanediaminonickel (*meso*-NiSaldMe-3dOEt),
- *N, N'*-dimethyl-*N, N'*-bis(3-methylsalicylidene)-2,3-butanediaminonickel (α, α -dMe-NiSalen-3dMe),
- *N, N'*-dimethyl-*N, N'*-bis(3-methylsalicylidene)-2,3-butanediaminonickel (α, α -dMe-CoSalen-3dMe),
- 2,3-phenyl-*N, N'*-bis(salicylidene)-2,3-butanediaminonickel (NiSalophen),
- 2,3-phenyl-*N, N'*-bis(salicylidene)-2,3-butanediaminocobalt (CoSalophen).

Furthermore, the applicability of these catalysts may be extended to other substrates or electrochemical processes, such as water splitting or CO₂ reduction. Further studies on the stability of catalysts under real-system-mimicking conditions and the employment of these NPs in EFC or UFC will be important steps towards the practical application of these NPs in the development of sustainable technologies for energy conversion and environmental remediation.

5 References

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Appendix

A1 The NMR spectra

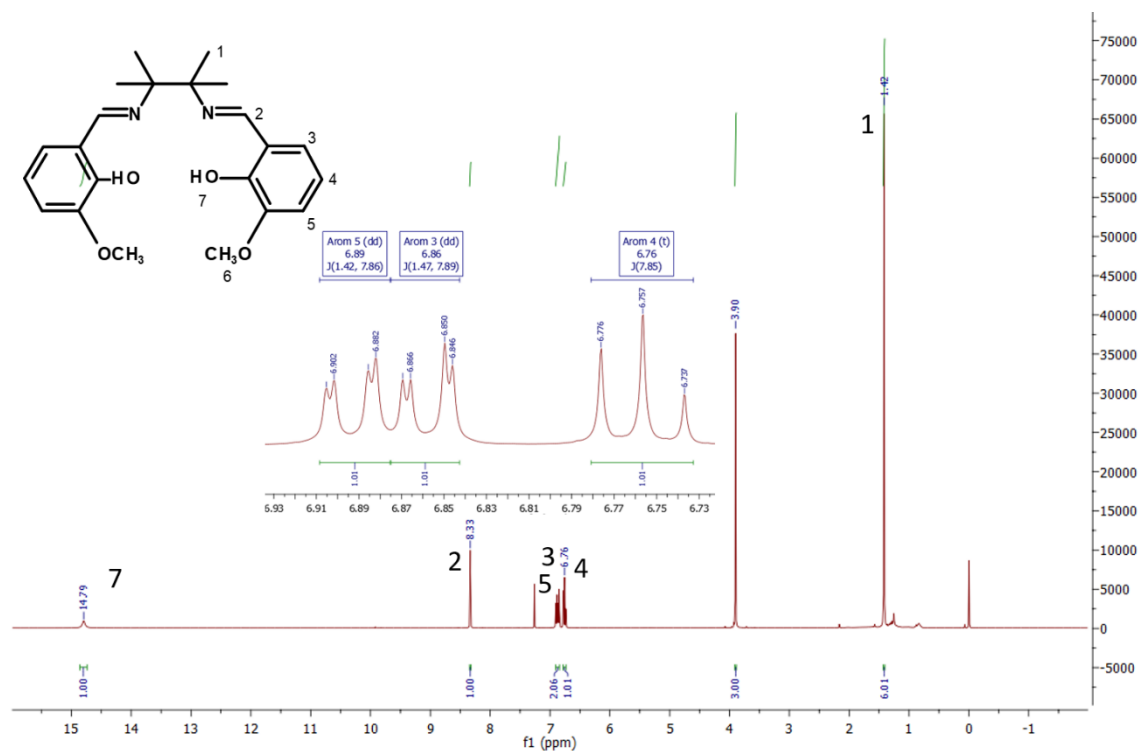


Figure A1-1. ^1H -NMR spectrum of SaltMe-3dOMe in CDCl₃.

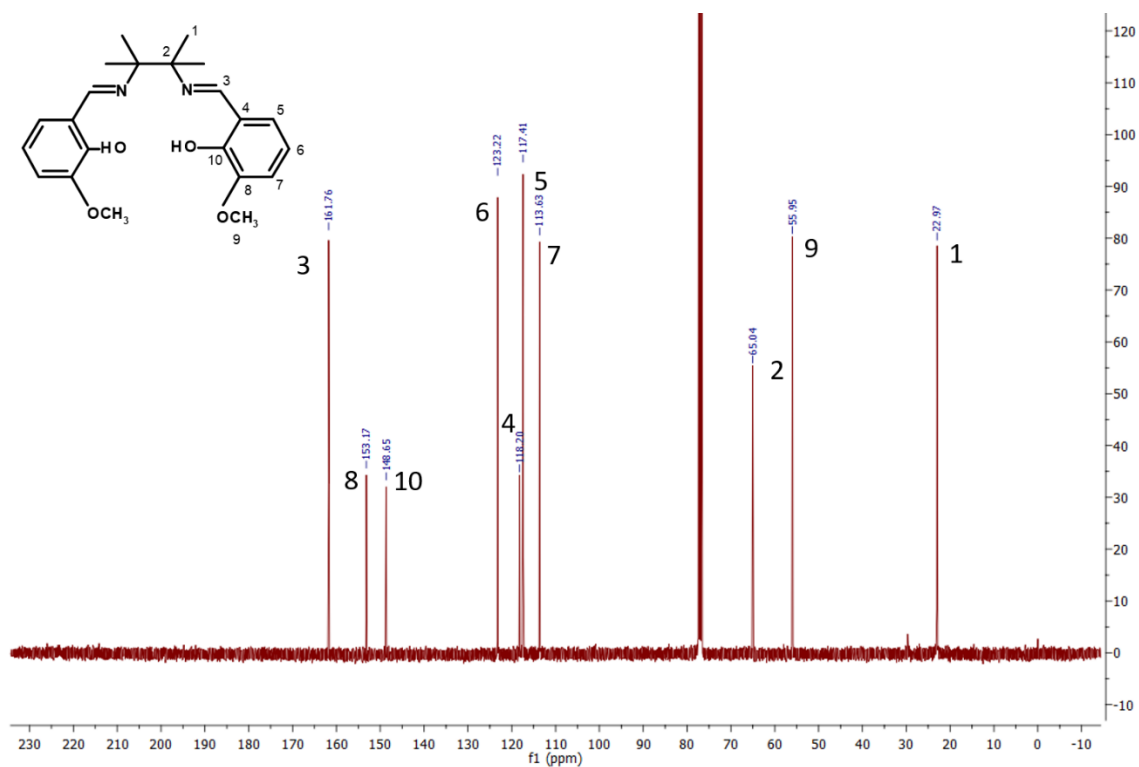


Figure A1-2. ^{13}C -NMR spectrum of SaltMe-3dOMe in CDCl_3 .

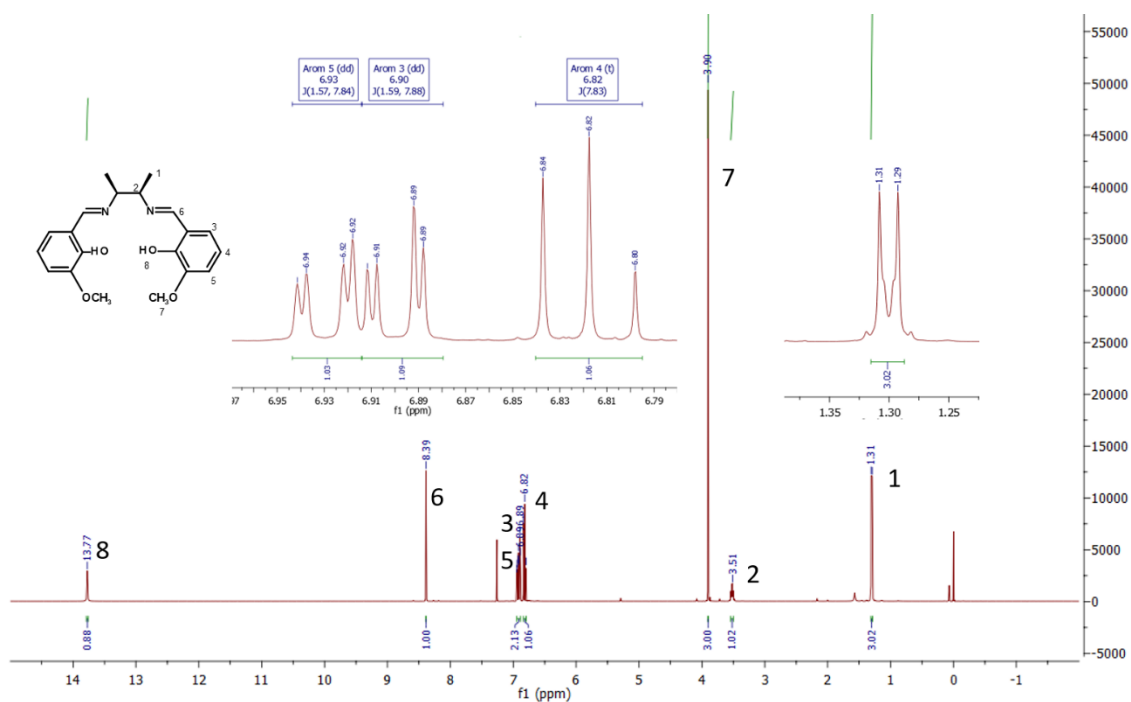


Figure A1-3. ^1H -NMR spectrum of *meso*-SaldMe-3dOMe in CDCl_3 .

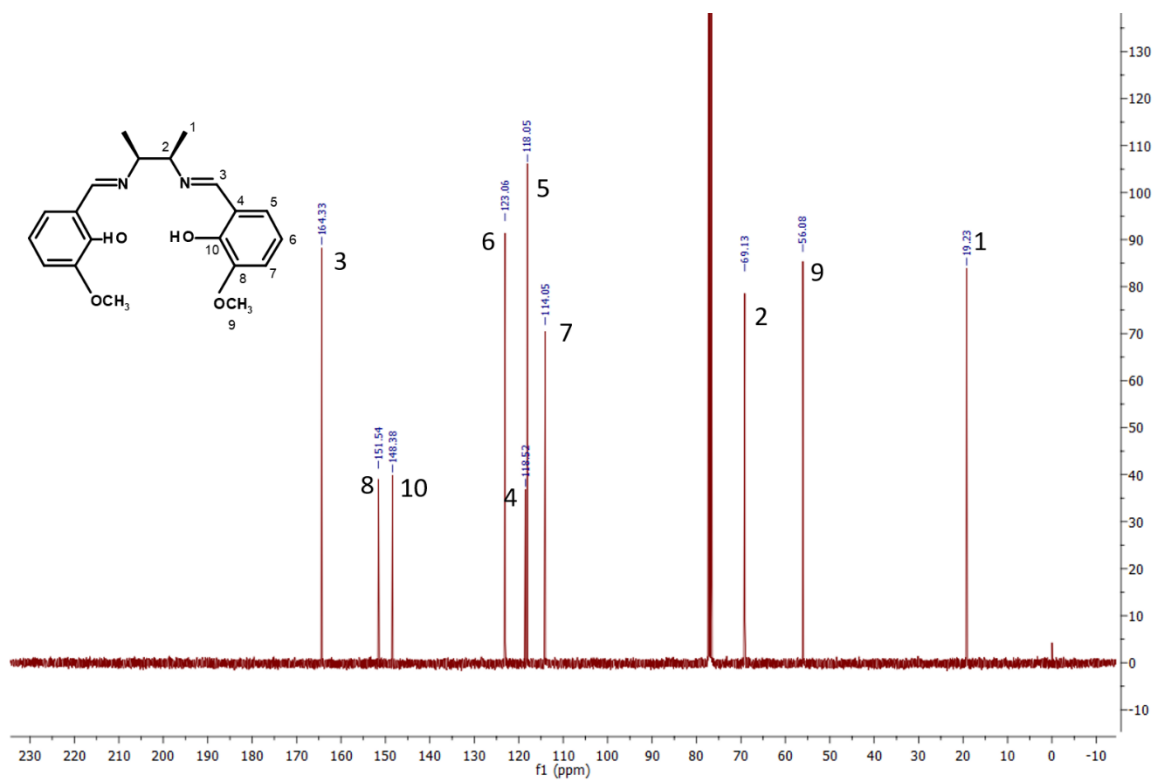


Figure A1-4. ^{13}C -NMR spectrum of *meso*-SaldMe-3dOMe in CDCl_3 .

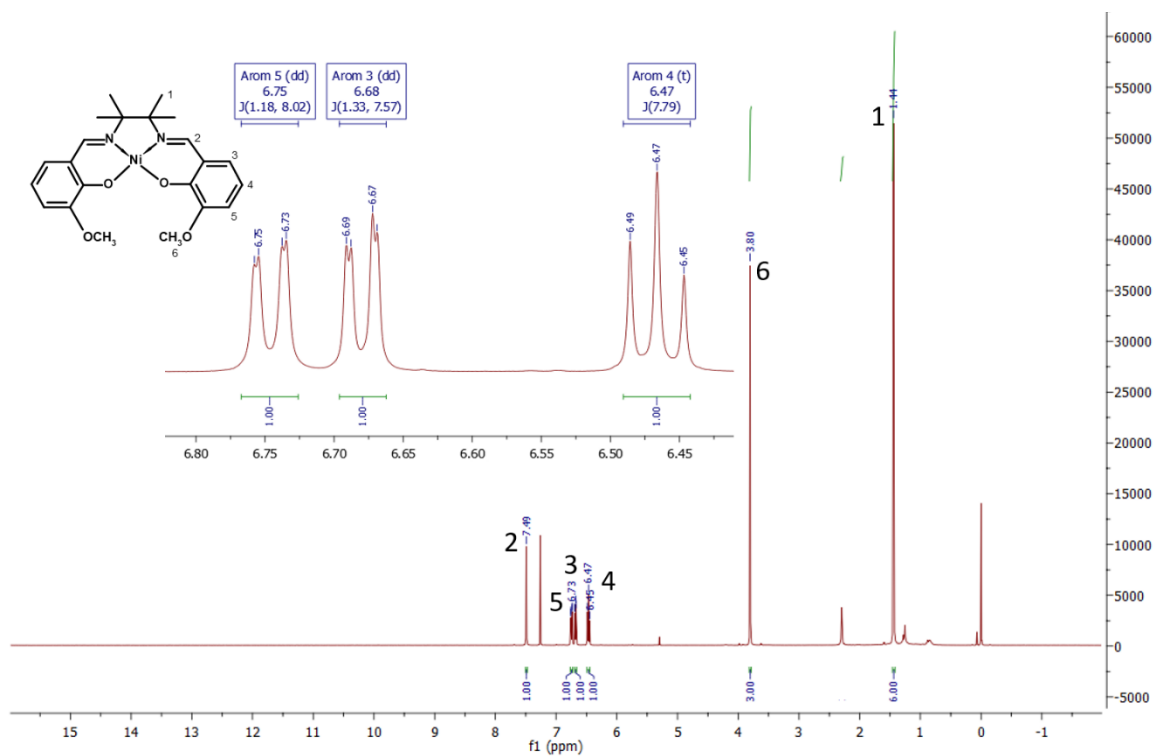


Figure A1-5. ^1H -NMR spectrum of NiSaltMe-3dOMe in CDCl_3 .

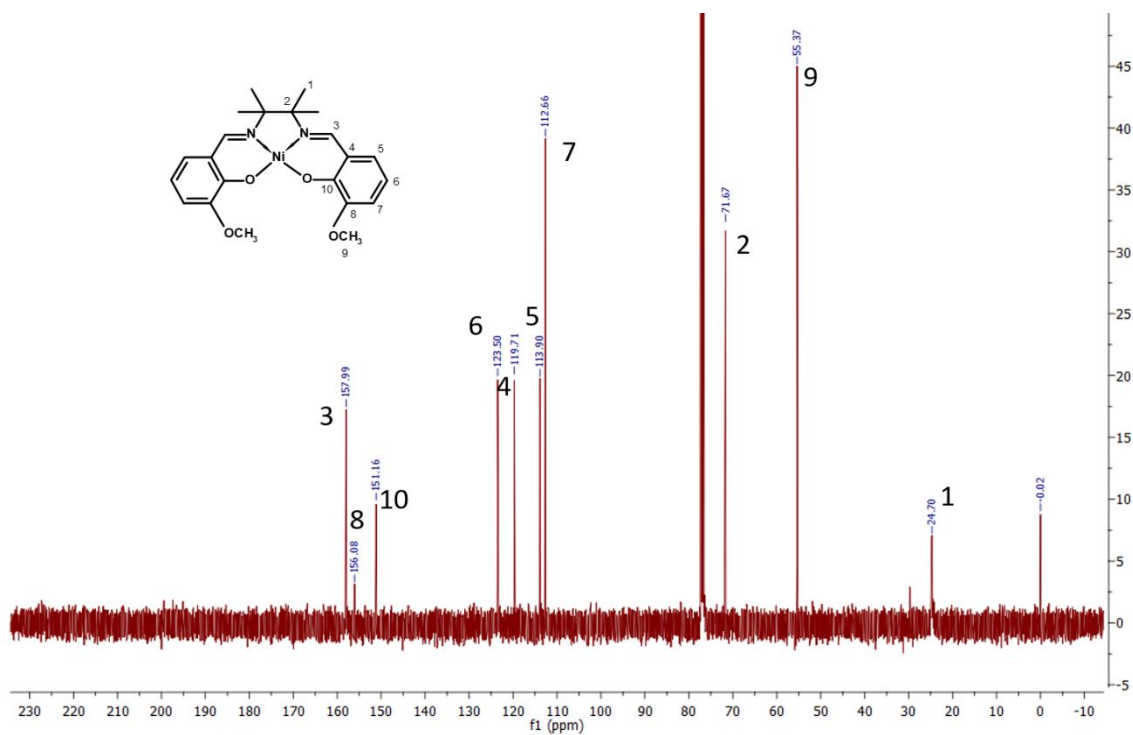


Figure A1-6. ^1H -NMR spectrum of NiSaltMe-3dOMe in CDCl_3 .

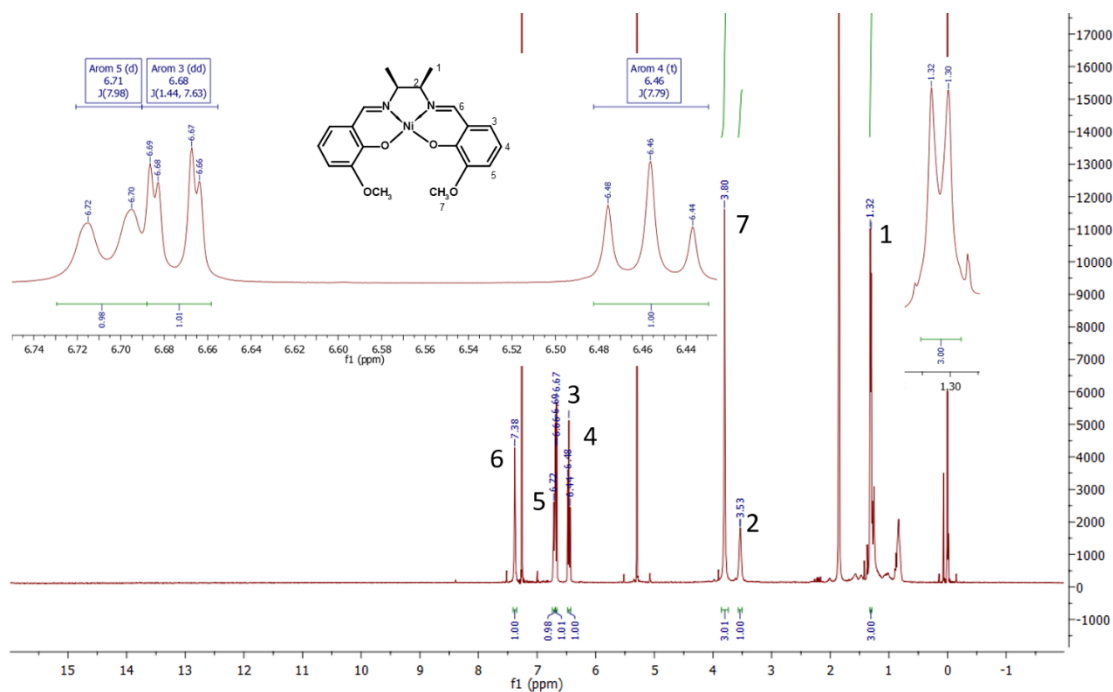


Figure A1-7. ^1H -NMR spectrum of *meso*-NiSaldMe-3dOMe in CDCl_3 .

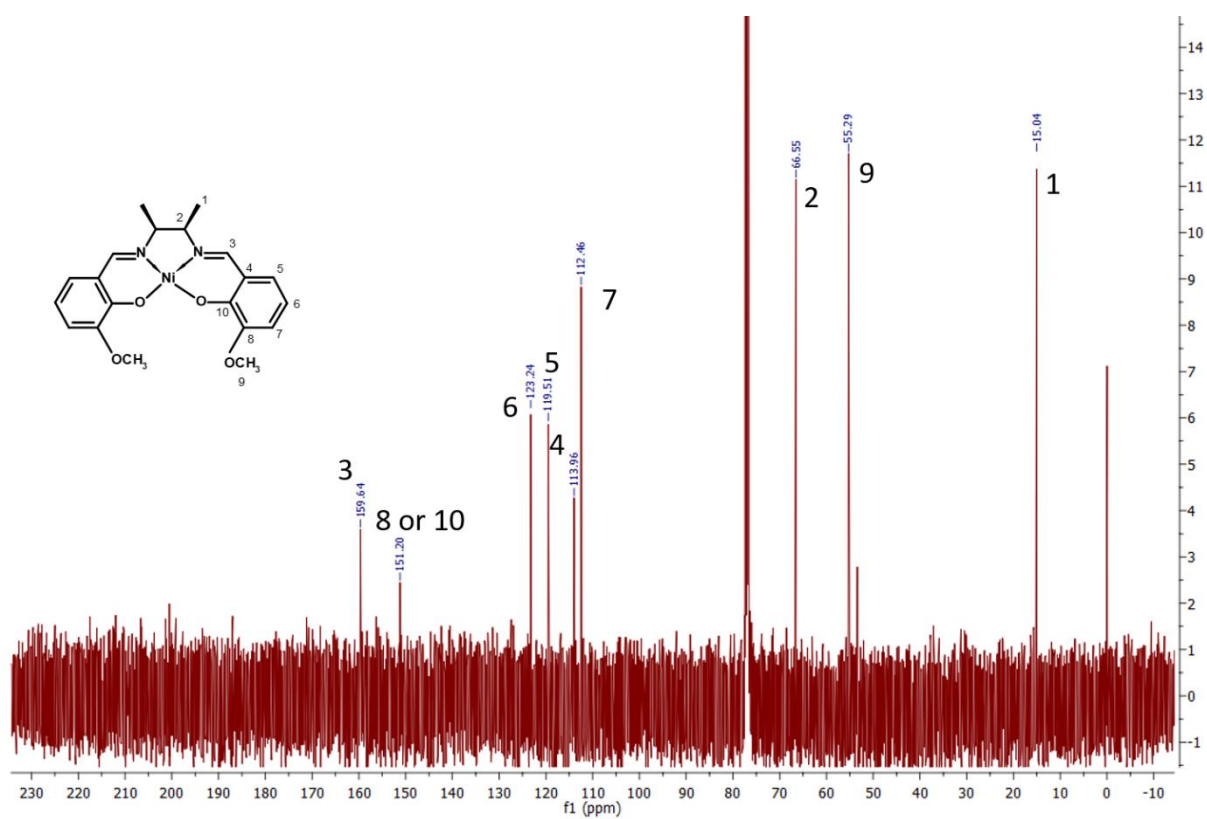


Figure A1-8. ^{13}C -NMR spectrum of *meso*-NiSaldMe-3dOMe in CDCl_3 .

A2 Acknowledgment to Publishers

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Figure 3.1-3, Figure 3.1-4, Figure 3.1-8.

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Figure 3.3-5, Figure 3.3-6, Figure 3.3-7, Scheme 3.3-1



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