Tailor-designed nanowire-structured iron and nickel oxides on platinum catalyst for formic acid electro-oxidation

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This investigation is concerned with designing efficient catalysts for direct formic acid fuel cells. A ternary catalyst containing iron (nano-FeO\textsubscript{x}) and nickel (nano-NiO\textsubscript{x}) nanowire oxides assembled sequentially onto a bare platinum (bare-Pt) substrate was recommended for the formic acid electro-oxidation reaction (FAOR). While nano-NiO\textsubscript{x} appeared as fibrillar nanowire bundles (ca. 82 nm and 4.2 \( \mu \)m average diameter and length, respectively), nano-FeO\textsubscript{x} was deposited as intersecting nanowires (ca. 74 nm and 400 nm average diameter and length, respectively). The electrocatalytic activity of the catalyst toward the FAOR depended on its composition and loading sequence. The FeO\textsubscript{x}/NiO\textsubscript{x}/Pt catalyst exhibited ca. 4.8 and 1.6 times increases in the catalytic activity and tolerance against CO poisoning, respectively, during the FAOR, relative to the bare-Pt catalyst. Interestingly, with a simple activation of the FeO\textsubscript{x}/NiO\textsubscript{x}/Pt catalyst at \(-0.5 \text{ V vs. Ag/AgCl/KCl (sat.) in 0.2 mol L}^{-1} \text{ NaOH}, \) a favorable Fe\textsuperscript{2+}/Fe\textsuperscript{3+} transformation succeeded in mitigating the permanent CO poisoning of the Pt-based catalysts. Interestingly, this activated a-FeO\textsubscript{x}/NiO\textsubscript{x}/Pt catalyst had an activity 7 times higher than that of bare-Pt with an ca. \(-122 \text{ mV shift in the onset potential of the FAOR}. \) The presence of nano-FeO\textsubscript{x} and nano-NiO\textsubscript{x} enriched the catalyst surface with extra oxygen moieties that counteracted the CO stripping and electronically facilitated the kinetics of the FAOR, as revealed from CO stripping and impedance spectra.

1. Introduction

Society is currently confronted with a difficult task; replacing traditional fossil fuels with renewable resources. Direct liquid fuel cells (DLFCs) have sparked widespread interest in research and industry as a very promising technology for resolving the worldwide environmental and energy crises.\textsuperscript{1,2} Among the several studied fuel cells (FCs), direct formic acid fuel cells (DFAFCs) appear to be promising as alternative power sources for portable electronic applications and in transportation due to their high energy density (\(~1.4 \text{ kWh kg}^{-1}\)), high theoretical open circuit potential (OCP \(~1.48 \text{ V})\), fast oxidation kinetics and cell efficiency.\textsuperscript{3,4} This is in addition to the utilization of a superior liquid fuel with high safety, low toxicity, low-flammability, ready availability, ambient temperature operability and low fuel crossover flux through Nafion membranes.\textsuperscript{5-9}

The most significant factors that influence the final output of DFAFCs are the electrocatalysts for both the anode and cathode electrodes, where Pt and Pd-based catalysts have been extensively studied due to their outstanding catalytic activity and long-term stability.\textsuperscript{7,9} Formic acid (FA) is one of the smallest organic molecules likely to be used, with only two electrons shared. Thus, it has been used as a model molecule in the study of the oxidation of other organic compounds with more intricate structures and oxidation mechanisms. Despite several efforts devoted to the research of the oxidation of these compounds, the overpotentials of the oxidation reaction are still far too high for large-scale practical application. Therefore, better electrocatalysts with lower overpotentials should be developed in order to optimize the fuel cell system’s overall energy efficiency.\textsuperscript{11} The reaction mechanism is an important piece of knowledge for the development of improved electrocatalysts. Knowing the intricacies of the reaction process will allow the development of new electrode materials able to speed up the reaction’s slowest steps, allowing the reaction bottlenecks to be overcome and higher efficiencies to be achieved.\textsuperscript{5,11} Because only two electrons are exchanged, the FA oxidation reaction (FAOR) is a comparatively simple reaction. In fact, only the cleavage of two bonds is needed for full oxidation to CO\textsubscript{2}: an O–H bond and an H–C bond. This second cleavage is possibly the most difficult stage, but pure metals (such as Pt, Pd and Ru)
are active for this stage because of their excellent properties for hydrogen adsorption.\textsuperscript{11,12} However, when this reaction was examined on platinum, a poisoning species, such as CO, was found to form. The formation of CO means the existence of unexpected problems in the process of oxidation. Because adsorbed CO is oxidized at high potentials, it prevents the reaction from taking place on the metal surface. Therefore, the oxidation mechanism involves two parallel routes: the direct formation of CO\textsubscript{2} from HCOOH at low potentials through a dehydrogenation step (desirable pathway) (HCOOH $\rightarrow$ CO\textsubscript{2} + 2H\textsuperscript{+} + 2e\textsuperscript{−}), and the indirect formation of CO via a chemical dehydration step, which will be further oxidized to CO\textsubscript{2} at higher potentials (HCOOH $\rightarrow$ CO\textsubscript{ads} + H\textsubscript{2}O $\rightarrow$ CO\textsubscript{2} + 2H\textsuperscript{+} + 2e\textsuperscript{−}).\textsuperscript{13-19}

Many catalysts have been reported for the FAOR in alkaline and acidic media. The noble metals are the most used electrocatalysts because of their superior activity. In fact, the FAOR on Pt and Pd electrodes has been the focus of growing interest since the 1960s.\textsuperscript{20} This is mostly owing to its importance in understanding methanol and formaldehyde oxidation, as well as the development of DFAFCs. However, difficult issues, such as limited catalytic activity on Pt at low potential, long-term instability (or deactivation) of Pd and Pt catalysts, degradation of carbon supports and the Nafion membrane, and water-CO\textsubscript{2} management in fuel cell stacks, impede DFAFC commercialization on a wide scale. Significant efforts are being made to solve these issues through different approaches, such as developing new designs of DFAFCs and preparing high efficiency anode catalysts.\textsuperscript{20,21} Particularly, Pt is regarded as the most suitable electrocatalyst among all metals due to its excellent stability. However, CO poisoning via the dehydrogenation pathway of the FAOR on the Pt surface degrades its catalytic activity, reducing its use. The combination of Pt-based intermetallic catalysts may improve the catalytic activity and durability for the FAOR.

In order to enhance the electrocatalytic activity, suppress poisoning by CO and increase the stability of the Pt catalyst toward the FAOR, several metals have been combined with Pt as intermetallic compounds, alloys, adatoms, or core–shell structures. The impact of other metals and/or metal oxides could be demonstrated by ensemble effects, electronic effects or a bifunctional mechanism. In this regard, Pt-based catalysts have made significant progress in direct oxidation activities by surface modification, shape engineering, and alloying with other metals such as Pd, Au, Cu, etc.\textsuperscript{5,20,22,23} Many other studies have been performed in order to use binary catalysts, such as PtM (M = Au,\textsuperscript{24,25} Bi,\textsuperscript{14} Co,\textsuperscript{26} Cu,\textsuperscript{27} Ni,\textsuperscript{28} Rh,\textsuperscript{29} Sn,\textsuperscript{30} Fe,\textsuperscript{31} Zr,\textsuperscript{32} Nb,\textsuperscript{33} etc.) and ternary catalysts such as PtM1M2 (M1M2 = RuAu,\textsuperscript{34} PdCu,\textsuperscript{25} CuFe,\textsuperscript{35} CuNi,\textsuperscript{36} AuCu,\textsuperscript{37} and BiPd\textsuperscript{7}). Furthermore, when modifying Pt surfaces with transition metal oxide nanostructures (M Ox), such as NiO\textsubscript{x},\textsuperscript{38,39} CoO\textsubscript{x},\textsuperscript{40} TiO\textsubscript{x},\textsuperscript{31} MnO\textsubscript{x},\textsuperscript{42,43} CuO,\textsuperscript{44} FeO\textsubscript{x},\textsuperscript{45,46} etc., the catalytic improvement achieved toward the FAOR was motivated by the so-called “bi-functional effect”, where the required oxygen atmosphere could easily be supplied by non-precious metal/s to facilitate the CO stripping at low overpotentials. Pt surface modification may also facilitate a change in the Pt work function in both circumstances (ensemble and bi-functional effects) to provide controlled tuning for Pt–FA and Pt–CO binding. In this study, the activity and stability of a new FeOx/NiOx/Pt catalyst for the FAOR was studied. The Pt surface was amended with peerless cheap and abundant metal oxides (FeOx and NiOx) that could effectively boost the kinetics of the FAOR and minimize the surface poisoning of Pt to allow DFAFCs to be scaled for practical use.

2. Experimental

2.1. Chemicals

All chemicals utilized in this work were of analytical grade and were used as received, with no prior purification. All solutions were prepared with double-distilled water. Nickel sulfate hexa-hydrate (NiSO\textsubscript{4}·6H\textsubscript{2}O), formic acid (HCOOH, FA), disodium hydrogen phosphate (Na\textsubscript{2}HPO\textsubscript{4}), hydrochloric acid (HCl), sodium hydroxide pellets (NaOH) and sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) were purchased from Sigma-Aldrich, whereas iron(II) sulfate heptahydrate (FeSO\textsubscript{4}·7H\textsubscript{2}O) and sodium sulfate (Na\textsubscript{2}SO\textsubscript{4}) were purchased from Riedel-de Haën and Merck, respectively.

2.2. Electrochemical measurements

Electrochemical tests, such as cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS), were performed in a constructed two-compartment three-electrode Pyrex glass cell. Polycrystalline platinum (d = 3.0 mm), platinum spiral wire and Ag/AgCl/KCl (sat.) served as the working, counter and reference electrodes, respectively. Even if not stated, all the potential readings in this study were taken in reference to the Ag/AgCl/KCl (sat.) electrode. All measurements were performed at room temperature (25 ± 1 °C) using an EG&G potentiostat (model 273) operated with E-Chem 270 software.

2.3. Catalyst preparation

The polycrystalline bare “pristine” Pt (bare-Pt or poly-Pt) electrode was mechanically polished with aqueous slurries of successively finer alumina powder, and subsequently sonicated and washed with double-distilled water. Then, the poly-Pt electrode was further electrochemically cleaned in 0.5 mol L\textsuperscript{−1} H\textsubscript{2}SO\textsubscript{4} solution by cycling the potential between −0.2 and 1.3 V at 100 mV s\textsuperscript{−1} until a characteristic CV for a clean poly-Pt electrode was obtained. The electrode modification with nickel oxide nanostructures (nano-NiOx) was achieved in three sequential steps. The first corresponded to the electrodeposition of metallic nickel (Ni) from 0.1 mol L\textsuperscript{−1} Na\textsubscript{2}SO\textsubscript{4} solution containing 1.0 mmol L\textsuperscript{−1} NiSO\textsubscript{4}·6H\textsubscript{2}O at a constant potential of −1.0 V for 120 s.\textsuperscript{38,39} After that, the metallic nickel was passivated to nickel oxide by cycling the potential from −0.5 to 1 V at 200 mV s\textsuperscript{−1} in 0.1 mol L\textsuperscript{−1} phosphate buffer solution (PBS, pH 7, prepared from 0.1 mol L\textsuperscript{−1} Na\textsubscript{2}HPO\textsubscript{4} and 0.1 mol L\textsuperscript{−1} HCl). Finally, the as-prepared electrode was activated by cycling the potential between −1 and 0.6 V at a scan rate of 200 mV s\textsuperscript{−1} for 25 cycles in 0.5 mol L\textsuperscript{−1} NaOH solution.

Fig. 1 exhibits CVs of 10 potential cycles in PBS (pH 7) for the passivation of deposited metallic Ni on the bare-Pt electrode.
For simplicity, only the first and tenth voltammograms are shown. A broad oxidative wave in the 1st CV corresponded to the active anodic dissolution and passivation of the electrodeposited metallic Ni synchronised between the various phases of nickel oxides. The following consecutive 9 CVs revealed a negligible anodic current, indicating a complete passivation of the surface layer of nickel during the first CV cycle. Interestingly, the absence of any significant reduction peaks in the cathode scan within the suitable potential domain indicated that the passive NiOx nanoparticles were stable within the potential range used and the specified pH. The electrodeposition of iron species was carried out by potential cycling (2 cycles) between −0.855 and −1.205 V at a scan rate of 100 mV s⁻¹ in 0.02 mol L⁻¹ FeSO₄·7H₂O solution. Next, the deposited iron was activated in 0.2 mol L⁻¹ NaOH aqueous solution at −0.5 V for 10 min, where iron oxide nanorods (nano-FeOx) were formed. To easily recognize the sequencing of the different catalytic ingredients and the post-treatment of the catalyst, abbreviations related to their developments were assigned. For instance, the a-FeOx/NiOx/Pt catalyst referred to the direct deposition of nano-NiOx onto the bare-Pt substrate followed by its passivation and activation. Then, nano-FeOx was deposited later onto the NiOx/Pt catalyst. The prefix “a-” denoted the further activation of nano-FeOx as described previously.

2.4. Materials characterization

The morphology and surface composition of the as-prepared Pt-based electrocatalysts were characterized by field-emission scanning electron microscopy (FE-SEM, Zeiss Ultra 60), at an acceleration voltage of 8 kV and a working distance of 2.8–3.2 mm, coupled with an energy dispersive X-ray spectrometer (EDX).

3. Results and discussion

3.1. Electrochemical and materials characterization

The electrochemical characterization was first used to detect the nature of the electroactive species on the various modified Pt electrodes. Fig. 2A compares CVs of the unmodified (a) bare-Pt and modified (b–f) NiOx/Pt, FeOx/NiOx/Pt, a-FeOx/NiOx/Pt, NiOx/FeOx/Pt and NiOx/a-FeOx/Pt catalysts, respectively, in 0.5 mol L⁻¹ NaOH solution. As can be clearly seen, the CV of the Pt electrode (curve a) exhibited typical characteristics of a clean poly-Pt electrode, with two peaks for the H_ads/des in the potential range from −1.0 to −0.65 V, together with another peak couple for the PtO/Pt transformation at −0.40 V. After modifying the Pt electrode with nano-NiOx, well-defined redox peaks at 0.32 and 0.42 V, corresponding to the Ni(II)/Ni(III) reversible transformation, were seen. In addition, a significant decrease was observed in the Pt surface area, which can easily be estimated from the lower peak intensities of the PtO reduction, Pt oxidation and H_ads/des peaks (curve b). A further modification with nano-FeOx resulted in the emergence of the distinctive well-defined redox peaks for Fe²⁺ ↔ Fe³⁺ at ca. −0.63 V (anodic scan) and −0.83 V (cathodic scan), curve c. Interestingly, the
Fe2+/Fe3+ peaks were shi

tlyst, with small negative shi

Fig. 2B shows the CVs for the same catalysts recorded in 0.5 mol L\(^{-1}\) \(\text{H}_2\text{SO}_4\) aqueous solution. The \(H_{\text{ads/des}}\) peaks, together with those of Pt → PtO oxidation and PtO → Pt reduction, were clearly seen for all catalysts. The polycrystalline nature of Pt was verified from the splitting of the \(H_{\text{ads/des}}\) peaks. The deposition of nano-NiO and/or nano-FeO on the Pt electrode reduced the exposed surface of the Pt, as inferred from the intensities of the \(H_{\text{ads/des}}\) and PtO/Pt peaks. The addition of nano-FeO to the NiO/Pt electrode resulted in the appearance of a well-defined redox peak couple in the region of 0.4 to 0.6 V, which might be attributed to Fe\(^{2+}/Fe^{3+}\) conversions.\(^{28}\) This peak couple was almost absent for NiO/Pt and a-FeO/NiO/Pt, but appeared for other catalysts. The absence of this peak in the case of a-FeO/NiO/Pt might be attributed to the detachment or phase transformation of FeOx on the Pt surface. After adding the modifiers (nano-NiO and/or nano-FeO) to Pt, the PtO/Pt peak shifted in the negative direction, especially in the case of the deposition of nano-FeO underneath nano-NiO (NiO/FeOx/Pt and NiO/a-FeOx/Pt electrodes), with an obvious overlapping of the PtO/Pt and Fe\(^{3+}/Fe^{4+}\) reduction peaks. The \(H_{\text{ads/des}}\) peaks with a monolayer adsorption charge of \(H_{\text{ads/des}}\) of 210 \(\mu\text{C cm}^{-2}\) at the Pt surfaces was, for accuracy purposes, used to compute the specific surface area of the catalyst,\(^{33}\) instead of the PtO → Pt peak, which might be overlapping with other reduction peaks of iron oxides.

FE-SEM imaging revealed the morphological characterization of the modified Pt electrodes. Fig. 3 shows typical FE-SEM micrographs of Pt before (a) and after (b, c and d) modification. The image of the NiOx/Pt (Fig. 3b) electrode showed that nano-NiOx was electrodeposited on the Pt surface in fibrillar nanowire bundles, with an average diameter of ca. 82 nm and length of 4.2 \(\mu\text{m}\). However, the nano-FeOx was electrodeposited on the NiOx/Pt electrode in intersected nanowires, with an average diameter of ca. 74 nm and length of 400 nm (Fig. 3c). Interestingly, the activation led to the emergence of many aggregates of nanowires (Fig. 3d). The elemental composition of the FeOx/NiOx/Pt electrode was identified by the EDX measurement, as shown in Fig. 4. It reflected that the catalyst contained Ni, Fe, O and Pt, with percentages of 9.97, 6.15, 48.51 and 35.37\%, respectively. The presence of O at such a high level was probably due to oxide formation, whereas the high extent of Pt resulted from the bare-Pt substrate. This indicated the successful deposition of the catalyst’s ingredients.

### 3.2. Electrocatalysis of the FAOR

The electrocatalytic performance of the modified electrodes toward the FAOR was investigated by recording CVs in 0.3 mol L\(^{-1}\) FA (pH 3.5) at a scan rate of 200 mV s\(^{-1}\) in the potential range from −0.2 to 1.0 V, (Fig. 5). It is worth mentioning that the stability of iron and nickel oxides decreases in highly acidic solutions.\(^{39,52}\) Therefore, the present study was conducted in a slightly acidic medium, pH = 3.5, located within the iron and nickel oxides’ stability domains. Additionally, a large (about one-third) amount of FA is ionized at this pH to formate anions.\(^{44}\) As such, the ionic conductivity is expected to be improved, along with a lower solution resistance.\(^{38,39}\) In general, there are two mechanisms suggested for the FAOR, as follows:

1. **Direct pathway mechanism:**

   \[
   \text{HCOOH} \rightarrow \text{H}_{(aq)}^+ + e^- + \text{HCOO}^* \quad (1)
   \]

   \[
   \text{HCOO}^* \rightarrow \text{CO}_2 + \text{H}_{(aq)}^+ + e^- \quad (2)
   \]
(2) Indirect pathway mechanism:

\[ \text{HCOOH} \rightarrow \text{H}_\text{aq}^+ + e^- + \text{COOH}^* \]  
(3) \[ \text{COOH}^* \rightarrow \text{CO}^* + \text{OH}^* \]  
(4) \[ \text{CO}^* + \text{OH}^* \rightarrow \text{CO}_2 + \text{H}_2 + e^- \]  
(5)

The direct pathway mechanism is dominant at low applied potentials (<0.25 V), resulting in CO₂ formation after two steps of proton/electron transfer, through an HCOO⁺ intermediate (eqn (1) and (2)). The indirect mechanism of the FAOR, prevalent at high applied potentials (>0.6 V), contributes to CO formation through a different intermediate, COOH⁺ (eqn (3) and (4)), and its subsequent oxidation to CO₂ (eqn (5)). The first (direct pathway) and second (indirect pathway) peak currents are symbolized as \( I_p \) and \( I_{p}^{\text{ind}} \) in the forward (positive-going) potential scan, respectively. In the backward scan, the FAOR continues on a clean Pt surface along with Pt dehydroxylation and perhaps CO₂ reduction, but generally the peak current \( I_b \) is overall anodic. The increase in the intensity of \( I_{p}^{\text{ind}} \) concurrent with the decrease of \( I_p \) indicates that the direct FAOR pathway becomes more favorable. Hence, the ratio of the two oxidation peaks \( \frac{I_{p}^{\text{ind}}}{I_p} \) represents how favorable it is for the FAOR to occur via the direct pathway (or the improvement in the overall catalytic efficiency of the FAOR) for a particular catalyst. Fig. 5 shows the CVS depicting and comparing the specific activities for the bare-Pt, NiOₓ/Pt, FeOₓ/NiOₓ/Pt, a-FeOₓ/NiOₓ/Pt, NiOₓ/FeOₓ/Pt and NiOₓ/a-FeOₓ/Pt catalysts. The \( I_{p}^{\text{ind}} \) of the catalysts followed this order: a-FeOₓ/NiOₓ/Pt (28.0 mA cm⁻²) > FeOₓ/NiOₓ/Pt (22.0 mA cm⁻²) > NiOₓ/FeOₓ/Pt (21.8 mA cm⁻²) > NiOₓ/a-FeOₓ/Pt (11.5 mA cm⁻²) > NiOₓ/FeOₓ/Pt (9.0 mA cm⁻²) > Pt (4.5 mA cm⁻²). Also, the catalytic activity (assessed using the \( \frac{I_{p}^{\text{ind}}}{I_p} \) ratio) of the catalysts followed this order: a-FeOₓ/NiOₓ/Pt (16.5, which is seven fold higher than that of bare-Pt) > FeOₓ/NiOₓ/Pt (11.0) > NiOₓ/a-FeOₓ/Pt (9.6) > NiOₓ/FeOₓ/Pt (9.5) > NiOₓ/Pt (7.5) > bare-Pt (2.3). The a-FeOₓ/NiOₓ/Pt and FeOₓ/NiOₓ/Pt catalysts had superior catalytic activities; outperforming all the other catalysts. The introduction of nano-NiOₓ and nano-FeOₓ could greatly improve the usage of Pt at the unit area level.

In fact, Fig. 5 indicates that the FAOR on the NiOₓ/Pt catalyst (curve b) showed an improved activity (compare \( I_p \)) relative to that of the bare Pt catalyst. Furthermore, the catalytic activities of the FeOₓ/NiOₓ/Pt and FeOₓ/Pt catalysts toward the FAOR were much better than those of the NiOₓ/Pt and bare-Pt catalysts, respectively. That is, \( \frac{I_{p}^{\text{ind}}}{I_p} \) for the FAOR on the a-FeOₓ/NiOₓ/Pt catalyst reached ca. 3.1 and 6.2 times higher than that obtained on the NiOₓ/Pt and bare-Pt catalysts, respectively, and the ratio \( \frac{I_{p}^{\text{ind}}}{I_p} \) of the FAOR increased from 2.3 (bare-Pt) to 7.5 (NiOₓ/Pt) to 11.0 (FeOₓ/NiOₓ/Pt) and 16.5 (a-FeOₓ/NiOₓ/Pt). The a-FeOₓ/NiOₓ/Pt and FeOₓ/NiOₓ/Pt catalysts exhibited greater FAOR current densities and lower onset potentials; indicating that nano-FeOₓ boosted the catalytic activity toward the direct FAOR. We believe that nano-NiOₓ and nano-FeOₓ could enhance the FAOR reaction via a bi-functional mechanism, in which the presence of nano-NiOₓ and/or nano-FeOₓ enriched the catalyst’s surface with extra oxygen moieties that facilitated the FAOR. Also, the EIS tests and CO stripping experiments (more details are provided below) further revealed that nano-FeOₓ enhanced the FAOR via an electronic effect, allowing a faster electron transport. Obviously, when the deposition order of the modifi ers was reversed (i.e., for the NiOₓ/FeOₓ/Pt catalyst), \( I_{p}^{\text{ind}} \) (21.8 mA cm⁻²), \( I_{p}^{\text{ind}} \) (9.5) and \( I_p \) (0.51) increased compared to those of the NiOₓ/Pt and bare-Pt electrodes. Yet, the catalytic enhancement \( \frac{I_{p}^{\text{ind}}}{I_p} \) of the former catalyst was still lower than that obtained with the FeOₓ/NiOₓ/Pt catalyst \( \frac{I_{p}^{\text{ind}}}{I_p} = 11.0 \), despite their \( I_p \) and CO tolerance being nearly the same. The data for the FAOR is summarized in Table 1. It is also interesting to note the competitive performance of the FeOₓ/NiOₓ/Pt catalyst, especially after activation, for the FAOR and CO tolerance when compared to the literature data for this reaction (see Table 2).41,45,56–60

3.3. Durability of the catalysts

The durability of the investigated catalysts toward the FAOR was tested by measuring current-time (\( I-t \)) relations of the FAOR at 0.3 V (Fig. 6). The initial rapid decrease in current demonstrated the poisoning of the electrocatalysts. The current densities of all Pt-modified catalysts were higher than that of the unmodified Pt electrode over continuous electrolysis for 3 h. For all catalysts, the sharp decrease in the current intensity ended with a steady-state current density. The a-FeOₓ/NiOₓ/Pt/GC catalyst current density remained nearly constant at ca. 4.0 mA cm⁻² after 3 h of continuous electrolysis, which was nearly fourfold higher than that (1.0 mA cm⁻²) of the bare-Pt electrode. Among all catalysts, the a-FeOₓ/NiOₓ/Pt catalyst maintained the highest current density over the time studied. This suggested that nano-FeOₓ enhanced the stability and poisoning tolerance of the Pt catalyst.

3.4. Electrochemical impedance spectroscopy (EIS)

The influence of additional modifi ers (such as nano-NiOₓ and/or nano-FeOₓ) on the charge transport kinetics and the interfacial properties was further investigated using EIS, which is a valuable tool for addressing the results of the FAOR. The charge transfer resistance \( R_{ct} \) of the prepared electrodes could be used to interpret the charge transfer kinetics of the FAOR. Table 3 compares the different EIS parameters: ohmic resistance \( R_o \), charge transfer resistance \( R_{ct} \), constant phase
Table 1 Variation of $i_{p}^{b}/i_{p}^{ind}$, $i_{p}^{ind}$, $i_{p}/i_{b}$ and $E_{onset}$ for the FAOR as evaluated from Fig. 5

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$i_{p}^{b}$ (mA cm$^{-2}$)</th>
<th>$i_{p}^{ind}$ (mA cm$^{-2}$)</th>
<th>$i_{b}$ (mA cm$^{-2}$)</th>
<th>$i_{p}^{b}/i_{p}^{ind}$</th>
<th>$i_{p}/i_{b}$</th>
<th>$E_{onset}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare-Pt</td>
<td>4.5</td>
<td>2.0</td>
<td>14.5</td>
<td>2.3</td>
<td>0.31</td>
<td>−74</td>
</tr>
<tr>
<td>NiOx/Pt</td>
<td>9.0</td>
<td>1.2</td>
<td>14.0</td>
<td>7.5</td>
<td>0.64</td>
<td>−174</td>
</tr>
<tr>
<td>FeOx/NiOx/Pt</td>
<td>22.0</td>
<td>2.0</td>
<td>45.0</td>
<td>11.0</td>
<td>0.49</td>
<td>−186</td>
</tr>
<tr>
<td>a-FeOx/NiOx/Pt</td>
<td>28.0</td>
<td>1.7</td>
<td>38.2</td>
<td>16.5</td>
<td>0.73</td>
<td>−196</td>
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<tr>
<td>NiOx/FeOx/Pt</td>
<td>21.8</td>
<td>2.3</td>
<td>42.5</td>
<td>9.5</td>
<td>0.51</td>
<td>−82</td>
</tr>
<tr>
<td>NiOx/a-FeOx/Pt</td>
<td>11.5</td>
<td>1.2</td>
<td>23.0</td>
<td>9.6</td>
<td>0.50</td>
<td>−80</td>
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</table>

Table 2 A comparison of the electrocatalytic activity ($I_{p}/I_{p}^{ind}$) and CO tolerance ($I_{b}/I_{b}^{ind}$) toward the FAOR for different catalysts

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$I_{p}/I_{p}^{ind}$</th>
<th>$I_{b}/I_{b}^{ind}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial Pt/C</td>
<td>0.16</td>
<td>—</td>
<td>54</td>
</tr>
<tr>
<td>Pt$<em>{11.1}$Ni$</em>{88.9}$/C</td>
<td>0.33</td>
<td>—</td>
<td>54</td>
</tr>
<tr>
<td>Pt$<em>{10.9}$Au$</em>{0.1}$Ni$_{88.9}$/C</td>
<td>0.34</td>
<td>—</td>
<td>54</td>
</tr>
<tr>
<td>Pt black</td>
<td>0.24</td>
<td>0.11</td>
<td>55</td>
</tr>
<tr>
<td>Pt/C</td>
<td>0.29</td>
<td>0.20</td>
<td>55</td>
</tr>
<tr>
<td>PtPd/C</td>
<td>0.87</td>
<td>0.51</td>
<td>55</td>
</tr>
<tr>
<td>Pt/GC</td>
<td>0.60</td>
<td>0.19</td>
<td>56</td>
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<tr>
<td>Pt/MWCNTs-GC</td>
<td>7.5</td>
<td>0.45</td>
<td>56</td>
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<tr>
<td>NiOx/Pt/GC</td>
<td>3.33</td>
<td>0.40</td>
<td>57</td>
</tr>
<tr>
<td>Au/Pt/GC</td>
<td>3.44</td>
<td>0.54</td>
<td>58</td>
</tr>
<tr>
<td>Si-TiO$_2$/TiO$_2$ (700 °C)</td>
<td>10.0</td>
<td>0.67</td>
<td>41</td>
</tr>
<tr>
<td>FeOx/Pt</td>
<td>9.1</td>
<td>0.58</td>
<td>45</td>
</tr>
<tr>
<td>a-FeOx/Pt</td>
<td>17.4</td>
<td>0.70</td>
<td>45</td>
</tr>
<tr>
<td>FeOx/NiOx/Pt</td>
<td>11.0</td>
<td>0.49</td>
<td>This work</td>
</tr>
<tr>
<td>a-FeOx/NiOx/Pt</td>
<td>16.5</td>
<td>0.73</td>
<td>This work</td>
</tr>
</tbody>
</table>

Interestingly, the diameter of the semicircle for the a-FeOx/NiOx/Pt electrode was smaller than those obtained for the other prepared catalysts in this investigation. The $R_{ct}$ decreased for these catalysts in the following order: bare-Pt (78.1 k$\Omega$) > NiOx/Pt (ca. 37.0 k$\Omega$) > FeOx/NiOx/Pt (25.8 k$\Omega$) > a-FeOx/NiOx/Pt (15.2 k$\Omega$). This low $R_{ct}$ for the FAOR on the a-FeOx/NiOx/Pt catalyst was definitely an important element in boosting the reaction kinetics. The different CPE values correlated to the different numbers of active sites at the catalysts’ surface; an increase in CPE is directly proportional to an increase in the active sites at the catalyst’s surface and, in turn, its activity. Alternatively, when $n = 1$, the CPE can be considered as an ideal capacitor.

As expected, all catalysts exhibited a non-ideal behaviour for the double layer, perhaps due to a microscopic inhomogeneity at the catalyst/liquid interface.

Fig. 6 Current–time transients obtained during the FAOR for the (a) bare-Pt, (b) NiOx/Pt, (c) FeOx/NiOx/Pt and (d) a-FeOx/NiOx/Pt catalysts in 0.3 mol L$^{-1}$ FA (pH 3.5) at a potential of 0.3 V.

Table 3 Impedance parameters obtained during the FAOR for the bare-Pt, NiOx/Pt, FeOx/NiOx/Pt and a-FeOx/NiOx/Pt electrodes. The data are derived from the corresponding EIS spectra (Fig. 7)

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$R_{ct}$ [k$\Omega$]</th>
<th>$R_{ct}$ [k$\Omega$]</th>
<th>CPE [\mu F cm$^{-2}$]</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare-Pt</td>
<td>0.354</td>
<td>78.10</td>
<td>1.189</td>
<td>0.9323</td>
</tr>
<tr>
<td>NiOx/Pt</td>
<td>0.319</td>
<td>36.97</td>
<td>5.177</td>
<td>0.7632</td>
</tr>
<tr>
<td>FeOx/NiOx/Pt</td>
<td>0.975</td>
<td>25.80</td>
<td>3.461</td>
<td>0.8207</td>
</tr>
<tr>
<td>a-FeOx/NiOx/Pt</td>
<td>0.238</td>
<td>15.20</td>
<td>15.880</td>
<td>0.8351</td>
</tr>
</tbody>
</table>

Fig. 7 Nyquist and Bode plots of the FAOR for the (a) bare-Pt, (b) NiOx/Pt, (c) FeOx/NiOx/Pt and (d) a-FeOx/NiOx/Pt catalysts in 0.3 mol L$^{-1}$ aqueous FA (pH 3.5) at open circuit potential.
Pt electrode, the CO stripping voltammogram of the NiO current density of 2.8 mA cm\(^{-2}\) was detected for the bare-Pt electrode at 0.71 V, with a peak yielding the oxidation peaks displayed in Fig. 8. A sharp peak surfaces of the bare-Pt, NiO respectively. This suggested higher CO tolerance of the FeO via both the bi-functional and electronic means that nano-FeO from the slightly negative shift in their peak potentials. This enrichment the catalyst surface with extra oxygen moieties that facilitated the FAOR, especially after activation.

### Conflicts of interest

There are no conflicts to declare.

### References


34 X. Hu, J. Zou, H. Gao and X. Kang, *J. Colloid Interface Sci.*, 2020, 570, 72–79.


