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Nickel Iron Diselenide for Highly Efficient and Selective

Electrocatalytic Conversion of Methanol to Formate

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Abstract

The electrooxidation of methanol to formate is an example of the potential use of renewable energies to add value to a biosourced chemical commodity. Additionally, methanol electrooxidation can replace the sluggish oxygen evolution reaction for hydrogen evolution or the electroreduction of other biomass-derived intermediates. Here, we demonstrate a noble metal-free catalyst, Ni_{1-x}Fe_xSe₂, with a high potential for an efficient and selective methanol conversion to formate. At its optimum composition, Ni_{0.75}Fe_{0.25}Se₂, this diselenide is able to produce 0.47 mmol cm⁻² h⁻¹ of formate at 50 mA cm⁻² with a Faradaic conversion efficiency of 99 %. We further demonstrate that Ni_{1-x}Fe_xSe₂-based catalysts are able to continuously work for over 50,000 s with a minimal loss of efficiency, delivering initial current densities above 50 mA cm⁻² and 2.2 A mg⁻¹ in a 1.0 M KOH electrolyte with 1.0 M methanol at 1.5 V vs. RHE.

Keywords: electrocatalysis; methanol oxidation reaction; selenide; nanoparticle; formic acid; biorefinery; biomethanol; formate

Introduction

Electrochemistry can play an important role in future biorefineries by allowing the valorization of biomass-derived chemicals using renewable energies such as wind and solar. It is becoming evident that the electrocatalytic reforming of biomass-derived chemicals is a potential cost effective, CO_2 -neutral and clean approach to produce hydrogen, biofuels, and value-added chemicals, and it can be even a convenient approach to store renewable energy in chemical bonds.[1–3]

Methanol is the most used commodity chemical. It can be obtained from CO_2 and different forms of biomass, including municipal, agricultural and forest waste. Methanol is used as a fuel in direct methanol fuel cells, but also as precursor or building block for the synthesis of other chemicals.[4] Currently, close to one million tons of formic acid are produced every year from the combination of methanol with CO at high pressure and the hydrolysis of the resulting methyl formate.[5] This is a cost-effective process because the price per metric ton of formate is a fourfold higher than that of methanol.[6,7] Formate is an essential and highly versatile chemical in many sectors, including chemical, textile, rubber, leather, pharmaceutic and printing industries. Formic acid can be also used as a fuel in direct formic acid fuel cells and for hydrogen storage.[8–11]

Among the possible alternative strategies to produce formate, the electrooxidation of (bio)methanol has several advantages, including a high energy efficiency, a potential high selectivity, the use of ambient pressures and temperatures, the potential use of electricity from renewable energy sources, its rapid activation and deactivation that allows using surplus energy when it becomes available, the scalability of the process, and its potential coupling with electroreduction reactions to generate hydrogen or other valuable fuels or chemicals.[10–14] The methanol oxidation reaction (MOR) to formate could be even coupled to the oxygen reduction reaction to cogenerate electricity.[15]

As a drawback, the electrochemical oxidation of methanol generally relies on noble metal-based and thus high cost electrocatalysts, which limits application at an industrial scale.[16,17] Recently, a great deal of effort has been devoted to the development of Ni- and

Co-based catalysts for the MOR.[18] Ni-based catalysts are characterized by particularly outstanding performances in alkaline media. This high performance is correlated with the surface oxidation of Ni to NiOOH, which is considered the MOR active phase.[19–25] Using *in-situ* infrared spectroscopy together with nuclear magnetic resonance spectroscopy, we recently demonstrated a 100% electrochemical conversion of methanol to formate on branched Ni₃C particles.[26] Other groups have demonstrated the combination of Fe and Ni to allow efficient MOR with current densities up to 1.71 A mg⁻¹ at 1.58 V vs. RHE, well above the values obtained for elemental Ni and Fe catalyst.[27] Besides, nickel selenide nanowires grown on nickel foil were demonstrated to deliver much higher current densities than the respective metal, oxide and sulfide, while at the same time showing an excellent stability.[28]

We take advantage of recent advances in the field to develop a higher performance catalyst for the cost effective methanol oxidation to formate. We present here an electrocatalysts based on bimetallic nickel-iron diselenide nanorods produced at low temperature in solution. The Ni/Fe ratio within the nanorods is tuned through the full Ni/Fe range to determine the optimum composition. The performance of these materials toward the electrocatalytic oxidation of methanol to formate is analyzed and its activity, selectivity and stability is determined.

Experimental Section

Chemicals. Nickel (II) acetylacetonate (Ni(acac)₂, 96%), iron (III) acetylacetonate (Fe(acac)₃, >99%), selenium powder (Se, 200 mesh 99.5%), and oleylemine (OAm, C₁₈H₃₇N, 80-90%) were purchased from Acros Organics. Potassium carbonate (K₂CO₃, 99.5%), potassium bicarbonate (KHCO₃, 99.7%), 1,2-ethanedithiol (EDT, HSCH₂CH₂SH, >98%), potassium hydroxide (KOH, 85%), oleic acid (OAc, C₁₈H₃₄O₂, 99%), carbon black (CB, Vulcan XC72), and Nafion (10 wt.%, perfluorinated ion-exchange resin, dispersion in water) were purchased from sigma Aldrich. Analytical grade hexane and ethanol were obtained from various sources. MilliQ water (18.2 MΩ·cm) was used for ink preparation and IC measurements. All chemicals were used as received, without any purification.

Ni_{1-x}Fe_xSe₂ precursor. To prepare the precursor required to produce 0.2 g of Ni_{1-x}Fe_xSe₂NRs, (1-x) of mM Ni(acac)₂, x mM of Fe(acac)₃, and 2 mM of Se powder were placed within a glass vial. Then 5 mL of OAm and 0.5 mL of EDT were added while stirring. Upon EDT incorporation, the color of the solution immediately turned from transparent to light yellow. The mixture was stirred for 2 h at 50 °C. The obtained precursor was then filtered through a 0.2 μ m filter before using. All the processes were carried out inside an argon-filled glove box.

Ni_{1-x}**Fe**_x**Se**₂ **NRs.** 20 ml of OAm was placed in a 50 ml three-neck flask and kept under vacuum first at room temperature for 20 min and then at 80 °C for 30 min to obtain a clear solution and remove low boiling point impurities. Afterward, the solvent was heated to 220 °C under Ar, and at this point the Ni_{1-x}Fe_xSe₂ precursor solution was injected into the flask. Upon injection, temperature dropped to ~210 °C. The mixture was allowed to recover the 220 °C and maintained at this temperature for 10 min. Afterward, the solution was rapidly cooled, ~80 °C/min, to room temperature using a water bath. During cooling, when the flask reached ~70 °C, 2 ml of OAc were added to replace the weakly bound OAm molecules. At ambient temperature, the crude solution was mixed with 10 ml of hexane and the product was isolated by centrifugation at 8000 rpm for 5 min. Particles were then dispersed again in hexane and precipitated one more time by centrifugation in the presence of ethanol. The NPs were finally re-dispersed in hexane and kept in the glovebox until their posterior use.

Material characterization: The crystal structure of the materials was characterized by X-ray diffraction (XRD) using a Bruker AXS D8 Advance (Cu K radiation: $\lambda = 1.5106$ Å). Refinement of the laboratory diffraction patterns were obtained by the Rietveld method with the GSAS-II package. Scanning electron microscopy (SEM) measurements were performed on a Gemini 300 field emission scanning electron microscope (ZEISS, Germany) equipped with an AZtecOne UltimMax40 energy spectrometer. High-resolution transition electron macroscopy (HRTEM) together with scanning TEM (STEM) investigation was performed on a field emission gun FEI Tecnai F20 microscope. High angle annular dark-field (HAADF) STEM was combined with electron energy loss spectroscopy (EELS) in the Tecnai microscope by using a GATAN QUANTUM filter. X-ray photoelectron spectroscopy (XPS) analyses were conducted on a SPECS system. Fourier transform infrared spectroscopy (FTIR) analysis were performed on an Alpha Bruker FTIR spectrometer with a platinum attenuated total reflectance (ATR) single reflection module. Electron paramagnetic resonance (EPR) spectroscopy was conducted on a Bruker EMXplus instrument (Bruker, Germany) with a microwave frequency of 9.40 GHz at 100 K. Around 10 mg of sample was loaded in a quartz EPR tube for each EPR measurement.

Electrochemical characterization. Electrochemical performance was measured on a Bio-logic SP-200 potentiostat at room temperature. All measurements were carried out using a conventional three-electrode system: a Pt wire as counter electrode (CE), a 5 mm diameter glassy carbon as working electrode (WE) and an Ag/AgCl as reference electrode (RE). To prepare the WE, 5 mg NRs and 10 mg CB were dispersed in 3 ml of MilliQ water/ethanol (v/v = 1:1) and 100 µL of a 10 wt% Nafion. After vigorously sonicating for 1 hour, 3 µL of the prepared ink was drop-casted on a carefully cleaned glassy carbon (GC) electrode, and then dried naturally in open air. The prepared alkaline electrolyte was bubbled with high-purity N₂ gas for half an hour before exploring the electrocatalytic performance. Cyclic voltammetry (CV), chronoamperometry (CA), and chronopotentiometry (CP) techniques were applied to study the activity and stability of the electrocatalyst. The measured potential (E) vs. reversible hydrogen electrode (RHE) was obtained using the following equation:

$$E_{vs.RHE} = E_{Ag/AgCl} + E^0_{Ag/AgCl} + 0.059 \times pH$$

where $E_{Ag/AgCl}$ is the measured potential E vs. RHE, $E^{0}_{Ag/AgCl}$ is the potential of the RE vs. RHE (0.21 V according to the manufacturer's web site), and pH is the theoretical value of 1.0 M KOH.

Product quantification. The product of the methanol electrochemical oxidation was characterized by ion chromatography (IC, analysis lab). A freshly prepared 4.5 mM KCO₃ and 0.8 mM KHCO₃ solution was used as leachate solution. During the CP measurement at a constant current output, 0.5 mL solution was collected at the same time intervals and diluted into MilliQ water with a ratio of 1:19 for the IC measurement. The produced amount of the product was calibrated based on standard solution with known concentrations. Then, the Faradaic efficiency (FE) was calculated using the following equation:

$$FE(\%) = \frac{mol \ of \ product \times n \times F}{total \ charge \ passed} \times 100\%$$

where n is the electron transfer number and F is the Faradaic constant (96485 C mol⁻¹).

Results and discussion

Nickel iron diselenide, Ni_{1-x}Fe_xSe₂, particles were produced over their entire compositional range via a two-step solution-based approach. The process involved the dissolution of Ni and Fe acetylacetonates and Se powder in an EDT solution, and the subsequent reaction of the mixture in OAm at 220 $\$ (see scheme in Figure 1a and experimental section for details). The reaction product consisted of particles with elongated morphology, with an average width of ca. 10 nm and an average length of ca. 50 nm (Figures 1b and S1). The Ni/Fe ratio was tuned by varying composition of the initial precursor solution (Table 1). Because the measured composition was in good agreement with the nominal composition, in the following we use the later to refer to the different samples.



Figure 1. (a) Scheme of the solution-based approach used to prepare $Ni_{1-x}Fe_xSe_2$. (b) Representative TEM macrograph of $Ni_{0.75}Fe_{0.25}Se_2$ nanoparticles with elongated geometry.

XRD patterns obtained from NiSe₂ and FeSe₂ particles were properly indexed considering the cubic pa-3 and orthorhombic pnnm crystal structure, respectively (Figure 2a). Ni_{0.75}Fe_{0.25}Se₂ was found to crystalize in the cubic NiSe₂ phase. Rietveld refinement of the XRD pattern of this sample showed a unit cell with a=b=c of 5.9449 Å, slightly above the 5.9195 Å measured for NiSe₂ (Figure S2). When adding larger amounts of Fe, XRD peaks in the two-theta region of $28^{\circ}-38^{\circ}$ and $48^{\circ}-56^{\circ}$ became visible, evidencing the change from the cubic NiSe₂ to the orthorhombic FeSe₂ phase.

Ni _{1-x} Fe _x Se ₂	Atomic ratio by EDS (%)			Fe*
(x)	Ni	Fe	Se	(x)
0	33	0	67	0.00
0.25	22	7	71	0.24

Table 1. Nominal and EDS Ni/Fe/Se atomic ratio of the Ni_{1-x}Fe_xSe₂ NRs.

0.50	15	15	69	0.50
0.75	9	23	68	0.72
1.0	0	32	67	1.00

* The atomic amount of Fe (x) was calculated by fixing the Se composition at 2 in $Ni_{1-x}Fe_xSe_2$.

Figures 2bc and S3 display representative HRTEM micrographs and the indexed power spectra of $Ni_{0.75}Fe_{0.25}Se_2$ and $Ni_{0.50}Fe_{0.50}Se_2$ samples. In both cases, particles were imaged along their [010] zone axis. STEM-EELS chemical analyses showed Fe, Ni, and Se to be homogeneously distributed within the particles (Figure 2b). STEM-EELS quantitative analysis of the Ni and Fe content were in good agreement with SEM-EDS analysis, with the metal composition varying in the ranges 75-80% for Ni and 20-25% for Fe in $Ni_{0.75}Fe_{0.25}Se_2$ (Figure 2b), and in the range 45-55% for both elements in $Ni_{0.5}Fe_{0.5}Se_2$ (Figure S3a). HRTEM analysis confirmed the $Ni_{1-x}Fe_xSe_2$ crystal structure to change symmetry when increasing the Fe amount, from cubic NiSe₂ pa-3 with space group 205 to orthorhombic FeSe₂ pnnm, space group 58, in good agreement with XRD analyses (Figure 2a). According to HRTEM analysis, $Ni_{0.50}Fe_{0.50}Se_2$ already crystallized in the orthorhombic structure and its power spectrum could be simulated using orthorhombic FeSe₂ with a 50% replacement of Fe by Ni (Figure S3b).

High resolution XPS spectra of the Ni $2p_{3/2}$, Fe $2p_{3/2}$ and Se 3d regions of Ni_{0.75}Fe_{0.25}Se₂ are displayed in Figures 2c and S4. Figure S5 displays XPS data obtained from NiSe₂. The main contribution to the XPS spectra of the two metals provided from surface oxidized states, NiO_x and FeO_x, although bands corresponding to Ni and Fe within a selenide environment where also clearly visible.[29] Surface oxidation took place during sample handling and transportation, as commonly observed in related materials.[30,31] The Se 3d spectra also showed two well defined contributions associated to an oxide component and to Se within a metal selenide environment.[32] The addition of a second minor oxidized component was required to properly fit the experimental data. These XPS spectra are in good agreement with data published in previous nickel iron selenides reports.[33–35]



Figure 2. (a) XRD pattern of Ni_{1-x}Fe_xSe₂, Rietveld refinement of the Ni_{0.75}Fe_{0.25}Se₂ pattern (GOF = 1.27. $R_w = 9.44\%$) and scheme of the crystal structure of NiSe₂ and FeSe₂. (b) HAADF-STEM image and EELS-STEM maps for Ni_{0.75}Fe_{0.25}Se₂. Maps were obtained using the Fe L-edges at 708 eV (green), Ni L-edges at 855 eV (red) and Se L edge at 1436 eV (blue). Relative composition maps are also displayed. (c) HRTEM micrographs and indexed power spectra obtained from Ni_{0.75}Fe_{0.25}Se₂ particles. (d) Ni 2p_{3/2}, and Se 3d high resolution XPS spectra from Ni_{0.75}Fe_{0.25}Se₂. (e) EPR spectra of Ni_{1-x}Fe_xSe₂, labels indicate x.

EPR analysis was used to evidence the electronic interaction between Ni and Fe within $Ni_{1-x}Fe_xSe_2$. Typically, Fe^{3+} , Ni^{2+} , and Ni^0 have associated EPR signals, while Fe^{2+} , Fe^0 , and Ni^{3+} do not.[36–38] As displayed in Figure 2e, no obvious resonance signal was detected from $NiSe_2$ (black line). On the other hand, broad EPR signals were obtained for all the samples containing Fe, with the highest signal intensity being observed for the sample containing the lowest amount of Fe: $Ni_{0.75}Fe_{0.25}Se_2$. The fluctuation of the signal intensity and position from sample to sample revealed the change of the metal valences as a function of the Ni/Fe ratio and the existence of a strong interaction between the two metals.[38]

Prior to the electrocatalyst preparation, $Ni_{1-x}Fe_xSe_2$ particles were precipitated and redispersed multiple times using ethanol and hexane. FTIR spectroscopy displayed the final particles to contain minimal amounts of organics on their surface (Figure S6). Electrocatalysts were prepared by mixing the cleaned $Ni_{1-x}Fe_xSe_2$ particles with CB and Nafion in DI water and ethanol (see experimental section for details).

The electrochemical performance of Ni_{1-x}Fe_xSe₂-based electrodes was initially tested using a conventional three-electrode system in the potential window 1.0-1.7 V vs. RHE with a scan rate of 50 mV s⁻¹ in an Ar-bubbled 1.0 M KOH electrolyte solution (Figure 3a). During the forward scan, a first current density peak for NiSe₂ and Ni_{0.75}Fe_{0.25}Se₂ electrodes at around 1.392 V was attributed to the transformation of Ni(OH)₂ to NiOOH.[39] At a potential higher than ca. 1.55 V, a dramatic current rise associated to the production of oxygen was obtained. During the backward scan, the reduction peak at around 1.31 V, both for NiSe₂ and for Ni_{0.75}Fe_{0.25}Se₂, was associated to the Ni reduction Ni³⁺ \rightarrow Ni²⁺. Increasing the Fe composition, the redox peaks shifted positively and became less obviously, while no redox peaks were obtained with the FeSe₂ electrodes below the OER potential.



Figure 3. CV curves in 1.0 M KOH without (a) and in presence of 0.5 M methanol (b) in the potential range 1.0 - 1.7 V vs. RHE and at a scan rate of 50 mV s⁻¹.

When adding 0.5 M methanol in the alkaline media, a sharp rise in the current density for $NiSe_2$ and $Ni_{0.75}Fe_{0.25}Se_2$ electrodes was obtained at around 1.40 V, i.e. after NiOOH formation (Figure 3b). On the other hand, a moderate increase of current density was obtained for the three electrodes containing larger amounts of Fe. Figure S7 displays the dependence of the MOR current density at 1.5 V on composition, after subtracting the current density delivered in 1.0 M KOH. When increasing the Fe content, the current density increased from the 15.5mA obtained for NiSe₂ to the 57.6 mA cm⁻² for Ni_{0.75}Fe_{0.25}Se₂ electrodes, to later decrease to 10.9, and 1.8 mA cm⁻² for Ni_{0.5}Fe_{0.5}Se₂ and Ni_{0.25}Fe_{0.25}Se₂ electrodes, respectively. FeSe₂ electrodes delivered no MOR current.

Nyquist plots of the impedance response of a Ni_{0.75}Fe_{0.25}Se₂ electrode measured at 1.6 V and 1.5 V in 1.0 M KOH with the presence and absence of 0.5 M methanol are shown in Figure S8. At 1.6 V, where oxygen was effectively generated, this electrode exhibited a smaller semicircle in the presence of methanol (R_{ct} of 6.5 Ω) than in its absence (R_{ct} of 10.9 Ω). As listed in Table S1, the fitting results at 1.5 V indicated a clearly enhanced charge-transfer process in the presence of 1.0 M methanol with a R_{ct} of only 5.4 Ω , much smaller than that in 1.0 M KOH, 121.5 Ω . The improved impedance responses indicated that the electrooxidation of methanol was favored over the production of oxygen at the same potential.



Figure 4. Electrochemical kinetics of a $Ni_{0.75}Fe_{0.25}Se_2$ -based electrode in 1.0 M KOH. (a) CV curves in 1.0 M KOH in the non-faradaic potential range with a scan rate of 10-100 mV s⁻¹. (b) Linear fitting of the current as a function of scan rate. (c) CV curves in the potential range from 1.0 V to 1.60 V at a scan rate of 50 mV s⁻¹. The curve obtained from a NiSe₂-based electrode is also plotted as reference. (d) CV curves in the potential range from 1.0 V to 1.60 V to 1.60 W s⁻¹. (e) Linear fitting of the peak current as a function of the scan rate in the scan rate range from 10 to 50 mV s⁻¹. (f) Linear fitting of the peak current as a function of the square root of scan rate in the scan rate range from 60 to 100 mV s⁻¹.

The electrochemically active surface area (ECSA) of the catalysts was determined using the double-layer capacitance (C_{dl}) on the basis of CVs measured at a series of variable scan rates in the non-faradaic potential range.[40] Generally, C_{dl} can be calculated from the linear fit of the current (*i*) with the scan rate (v):

$$i_c = v C_{dl}$$

Then ECSA can be determined by dividing C_{dl} by the specific capacitance:

$$ECSA = C_{dl}/C_s$$

where C_s is 0.04 mF cm⁻² based on values reported for metal electrodes in aqueous alkaline solution.[41]

 $Ni_{0.75}Fe_{0.25}Se_2$ electrodes displayed the largest ECSA values among the series tested, 62.5 cm² g⁻¹, threefold above the value obtained for NiSe₂ electrodes, 18.75 cm² g⁻¹ (Figure S9). These values were below those reported for branched Ni₃C particles, 108.6 cm² g⁻¹, [26] and

 $Ni_{97}Bi_3$ aerogels, 176.6 cm² g⁻¹, [42] but well above those of branched $Ni_{0.75}Cu_{0.25}$, 0.12 cm² g⁻¹, [43] and NiO nanotubes, 36.25 m² g⁻¹. [44]

In the faradaic region, the potential difference between the Ni(OH)₂ \leftrightarrow NiOOH redox peaks (ΔE_p) is related to the electron transfer kinetics between the electrode surface and the active centers.[45] As shown in Figure 4c, Ni_{0.75}Fe_{0.25}Se₂ electrodes displayed the lowest ΔE_p , 65 mV compared with the 91 mV obtained for NiSe₂, demonstrating the addition of Fe within the NiSe₂ lattice to improve the reaction kinetics.

Figure 4d displays CV curves at different scan rates in the range 10-100 mV s⁻¹ for a $Ni_{0.75}Fe_{0.25}Se_2$ electrode. While the peak current increased with the scan rate, the anodic peak potential shifted positively and the cathodic negatively. Qualitatively similar changes in the peak current and potential were observed for NiSe₂ electrodes (Figure S10a). The shift of the peak potential is attributed to an electrochemical polarization and the limited reaction kinetics that control the formation of NiOOH species.[45]

The electrochemical performance of Ni-based electrodes is generally improved with the surface coverage of Ni(OH)₂/NiOOH redox species (I^*).[46] From the linear fit of the anodic and cathodic peak current (I_p) with the sweep rate (v) from 10 to 50 mV s⁻¹ in the potential range of 1.0-1.6 V, the surface coverage of redox species (I^*) was estimated using the following equation:

$$I_p = \left(\frac{n^2 F^2}{4RT}\right) A I^* v$$

where n is the number of transferred electrons (assumed to be 1), F is the Faraday constant (96,845 C mol⁻¹), R is the gas constant (8.314 J K⁻¹ mol⁻¹), T is absolute temperature (295 K) and A is the geometric surface area of the GC electrode (0.196 cm²).

Averaging the results obtained from the forward and reverse scans, I^* of Ni_{0.75}Fe_{0.25}Se₂ electrodes was 7.3×10^{-8} mol cm⁻² (Figure 4e), slightly larger than I^* obtained for NiSe₂, 5.7 $\times 10^{-8}$ mol cm⁻² (Figure S10b). These values of I^* were in agreement with those reported previously for NiCo₂Sn₂ (4.1 × 10⁻⁸ mol cm⁻²),[47] Ni₉₇Bi₃ (5.6 × 10⁻⁷ mol cm⁻²),[42] Ni-C-30 (8.9 × 10⁻⁸ mol cm⁻²),[48] and Ni nanoparticles (1.9 × 10⁻⁷ mol cm⁻²). [49]

We further investigated the electrochemical activities based on the proton diffusivity (D) within the electrodes according to the Randles–Sevcik equation.[50] For Ni-based electrodes, the proton diffusion is generally regarded as a rate-limiting step that controls the Ni(OH)₂ \leftrightarrow NiOOH redox reaction.[51] In the scan rate range 60-100 mV s⁻¹ (Figure 4f), the anodic and cathodic peak current (I_p) was found to be a linear function of the square root of scan rate ($v^{1/2}$), inferring a diffusion-limited redox reaction. Thus, the diffusion coefficient (D) could be determined from the following equation:

$$I_n = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2}$$

where n and C are the electron transfer number (assumed to be 1) and the initial concentration of redox species, respectively. Using this equation, the proton diffusion coefficient for the Ni_{0.75}Fe_{0.25}Se₂ electrode was estimated at 2.2×10⁻¹⁰ cm² s⁻¹, an order of magnitude above that of the NiSe₂ electrode, 5.7×10^{-11} cm² s⁻¹ (Figure S10c), which pointed at a much faster diffusion of the redox limiting specie in the sample containing Fe. The diffusion coefficient calculated for Ni_{0.75}Fe_{0.25}Se₂ was in the same order of magnitude as that of branched Ni₃C particles (6.0×10^{-9} cm² s⁻¹),[26] branched Ni_{0.75}Cu_{0.25} (2.9×10^{-8} cm² s⁻¹),[43] Ni-B nanoparticles on nanoporous Cu electrode (4.8×10^{-9} cm² s⁻¹),[52] and nanoporous Ni-Cu-P alloys (3.65×10^{-10} cm² s⁻¹).[53]



Figure 5. Performance of the $Ni_{0.75}Fe_{0.25}Se_2$ -based electrode. (a) CV curves in 1.0 M KOH electrolyte in the potentials range from 1.0 V to 1.5 V at a scan rate of 50 mV s⁻¹ with the

presence of different methanol concentration from 0.1 M to 1.0 M. (b) Current density at 1.5 V in 1.0 M KOH containing 0.1 M to 3.0 M methanol. (c) Logarithmic dependence of the current density at 1.50 V in 1.0 M KOH solution with the methanol concentration from 0.1 M to 3.0 M. (d) CP profile at a constant current of 5 mA in 1.0 M KOH containing 1.0 M methanol and CA response at 1.48 V during 10,000 s testing. (e) IC profile in 1.0 M KOH containing 1.0 M KOH containing 1.0 M methanol during 10,000 s CP testing (5 mA) obtained at 2,000 s intervals. (f) Calculated Faradaic efficiency for the methanol-to-formate conversion at 2,000 s, 4,000 s, 6,000 s, 8,000 s, and 10,000 s times during CP test.

Figure 5a displays CVs (50 mV s⁻¹) of Ni_{0.75}Fe_{0.25}Se₂-based electrodes in a 1.0 M KOH electrolyte containing different methanol concentrations, from 0.1 M to 1.0 M. The current density associated to the MOR clearly increased with the methanol concentration, until ca. 0.3 M. Figure 5b displays current density vs. methanol concentration at 1.5 V. The current density initially increased with the methanol concentration, from 28.6 mA cm⁻² at 0.1 M, up to 51.8 mA cm⁻² at 0.3 M, and it was stabilized at around this value for higher methanol concentrations, up to 3.0 M. A linear fit of the logarithmic dependence of the current density vs. methanol concentration range indicated the methanol reaction order to be ca. 0.6 (Figure 5c).

Averaging the current density obtained from 5 $Ni_{0.75}Fe_{0.25}Se_2$ -based electrodes fabricated from different batches of particles, we calculated a current density of 59.7 mA cm⁻² at 1.5 V, which decreased to 53.5 mA cm⁻² after subtracting the current density in 1.0 M KOH (Figure S11). This value corresponds to 2.2 A mg⁻¹ (considering the mass of catalyst loaded on the GC), which is the highest MOR activity reported for a Ni-based electrode to date (Table 2).

	Activities			
Electrocatalyst	Electrolyte	(1.5 V vs RHE)		Reference
		mA cm ⁻²	A mg ⁻¹	
Ni/rGO	1.0 M KOH + 1.0 M methanol		1.5	[54]
Ni-CNT/SiC	1.0 M NaOH + 1.0 M methanol	31.2	1.9	[55]
(110)-faceted Ni	1.0 M KOH + 1.0 M methanol	41.1	1.4	[49]
Ni/beta- zeolite	0.1 M NaOH + 0.1 M methanol	7.5	0.2	[56]
NiO layer/CNT	1.0 M KOH + 0.5 M methanol	56.7		[57]
defect-rich NiO	1.0 M KOH + 0.5 M methanol	24.3	0.1	[44]
NiO/Ni heterostructures	1.0 M KOH + 2.0 M methanol	9.4	1.8	[58]

Table 2. Electrocatalytic performance comparison between the $Ni_{0.75}Fe_{0.25}Se_2$ electrodes and other Ni-based electrodes previously reported

Ni ₂ Co ₂	1.0 M NaOH + 0.5 M methanol	18.5		[19]
Ni _{2.5} Co _{0.5} Sn ₂	1.0 M KOH + 1.0 M methanol	38.6	0.6	[47]
NiCo/NiO-CoO/carbon	0.5 M NaOH + 0.5 M methanol	75.6		[59]
NiMoO ₄	1.0 M KOH + 2.0 M methanol	11.2		[60]
Ni _{0.75} Cu _{0.25}	1.0 M NaOH + 0.5 M methanol	23.6	0.1	[43]
Cu-Ni/CNT	1.0 M NaOH + 3.0 M methanol		0.3	[21]
1D Cu/NiCu	1.0 M KOH + 1.0 M methanol	25.1	0.6	[61]
Fe-Ni core/shell	1.0 M NaOH + 1.0 M methanol	6.5	1.4	[27]
$Ni_{0.97}Bi_{0.03}$	1.0 M KOH + 1.0 M methanol		0.8	[42]
Ni-B amorphous alloy/Cu	1.0 M KOH + 0.3 M methanol	66.1		[52]
3D Ni-P-O	0.5 M KOH + 1.0 M methanol		1.1	[62]
Branched Ni ₃ C	1.0 M KOH + 1.0 M methanol	51.2	1.6	[26]
NiSe/Ni	1.0 M KOH + 0.5 M methanol	132		[28]
$Ni_{0.75}Fe_{0.25}Se_2$	1.0 M KOH + 1.0 M methanol	53.5	2.2	This work

Figure 5d displays results from CP test at 5 mA in a 1.0 M KOH electrolyte containing 1.0 M methanol. A relatively stable potential, in the range 1.45-1.47 V, was required to maintain a stable current during the 10,000 s test. Figure 5d displays the low current obtained during a CA test at 1.48 V in 1.0 M KOH without methanol, demonstrating the current measured during CP to be directly related to the methanol oxidation.

The reaction products were quantified by analyzing the ion type and concentration during CP test by means of IC (Figure 5d). As shown in Figure 5e, several peaks were identified at 2.7, 4.1, 5.2, 6.9, and 21 min, which were ascribed to water, F^- , HCOO⁻, Cl⁻, and SO₄²⁻ respectively. Notice how the largest peak corresponded to formate, which generation involved 4 electrons in the overall reaction in alkaline media:[6]

 $CH_3OH + 5OH^- \rightarrow HCOO^- + H_2O + 4e^-$

As displayed in the inset in figure 5e, the formate concentration increased with the CP time, i.e. with the total amount of charge flown (Table S1). From these values, the Faradaic efficiency of the methanol-to-formate conversion was calculated to be close to 99% (Figure 5f). In these conditions, the production rate of formate was 0.23 mmol cm⁻² h⁻¹.

The stability of $Ni_{0.75}Fe_{0.25}Se_2$ electrodes was further investigated by means of CP, CA and continuous CVs in 1.0 M KOH electrolyte with 1.0 M methanol. Figure 6a displays a CP

profile at 50 mA cm⁻². The initial voltage was 1.46 V, and after 50,000 s CP test this value increased by just ca. 50 mV. After this test, 1.27 mmol formate had been electrochemically produced through the injection of 500 C of charge, which corresponded to a Faradaic efficiency of 98.2% and a production rate of 0.47 mmol cm⁻² h⁻¹.

CA analysis at 1.50 V displayed the current density of the $Ni_{0.75}Fe_{0.25}Se_2$ electrode to gradually decrease. While a 27.4% lower current density was obtained after 50,000 s, the retained current density (38.9 mA cm⁻²) was still well above the initial current densities of most Ni-based MOR catalysts previously reported (Table 2). As shown in the inset of Figure 6b, after the long-term electrocatalytic process (50,000 s CA) in alkaline media and at high potential, the catalyst particle size and morphology remained constant.[63–65]

CV profiles showed a gradual current density decay in the potential window 1.0-1.5 V upon long term cycling (figure 6c). The current density at 1.5 V retained 91.9%, 83.9%, 74.0%, 67.7%, and 61.5% of the initial value after 200, 400, 600, 800, and 1000 cycles, respectively (Figure 6d).



Figure 6. Stability test of the $Ni_{0.75}Fe_{0.25}Se_2$ -based electrode in 1.0 M KOH with 1.0 M methanol. (a) CP profile during 50,000 s operation at a constant current density of 50 mA cm⁻² The IC profile obtained from the solution after completing the CP test is also plotted as inset.

(b) CA response at 1.5 V during 50,000 s test. The inset shows the morphology of the catalyst after the test. (c) Continuous 1,000 CVs cycling in the potential range of 1.0-1.5 V. (d) The corresponding current density change at the 200^{th} , 400^{th} , 600^{th} , 800^{th} , and 1000^{th} CV compared with the initial CV at 1.5 V.

Conclusion

In summary, we reported a fast solution-based route to produce nickel iron diselenide nanorods. The materials were thoroughly characterized and their performance toward MOR was tested. We found the incorporation of iron into the NiSe₂ structure to modify the material electronic structure and to significantly improve the electrocatalytic performance, including ECSA, surface coverage of active species for MOR, and diffusivity of limiting species in alkaline media. The optimal composition was found to be Ni_{0.75}Fe_{0.25}Se₂. Electrodes based on Ni_{0.75}Fe_{0.25}Se₂ nanorods delivered a current density up to 53.5 mA cm⁻², corresponding to 2.2 A mg⁻¹, in 1.0 M KOH electrolyte containing 1.0 M methanol at 1.5 V. These electrodes were able to produce 0.47 mmol cm⁻² h⁻¹ of formate at 50 mA cm⁻² with a Faradaic conversion efficiency of 99 % and to continuously work for over 50,000 s with a low efficiency loss. Taking into account the economic advantages of using a noble-metal-free catalyst, its high Faradaic efficiency, and ambient operation, the electrochemical conversion of methanol to formate might indeed become an efficient approach to add value to biomass-derived chemicals.

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Author contributions

The manuscript was contributed and authorized by all authors. C. Cui and A. Cabot conceived and guided the project, and supervised the work. J. Li designed the experiments, performed electrochemical measurements, and wrote the first draft. C. Xing and Y. Zhang produced the NRs, conducted XRD. M. C. Spadaro, T. Zhang, and J. Arbiol conducted structural and compositional NRs characterization by means of HRTEM and EELS, and discussed the results. Q. Wu and Y. Yu provided assistance to the EPR and IC measurement, respectively. S. He significantly joined the results discussion. J. Llorca measured and discussed XPS data. This manuscript was corrected and improved by all authors.

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Conflict of interest

The authors declare no competing financial interest.

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