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Enhancing Electrocatalytic Hydrogen Evolution by Nickel Salicylaldimine Complexes with Alkali Metal Cations in Aqueous Media

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New salicylaldimine nickel complexes, comprising only earth-abundant elements, have been developed for electrocatalytic hydrogen evolution in aqueous media. Second-sphere ether functionalities on the periphery of the complexes enhance the electrocatalytic activity in the presence of alkali metal cations. The electrocatalysts demonstrate improved performances especially in the economical and sustainable seawater reaction medium.

Global climate change has been widely attributed to the rampant consumption of fossil fuels and has stimulated recent efforts to develop alternative, more sustainable sources of fuels. An attractive solution is to develop artificial photosynthetic systems that can harvest sunlight, like a leaf, and store the solar energy in the form of chemical bonds in hydrogen (H₂) and oxygen (O₂) *via* water splitting. Energy storage is appealing since sunlight is intermittent. When alternative energy resources such as sunlight or geothermal energy can be efficiently converted into electricity, a critical challenge in creating a practical artificial photosynthetic system will be to develop commensurately efficient electrocatalysts for H₂ evolution from seawater.¹⁻⁴

Platinum (Pt) is a well-known electrocatalyst for the reduction of protons (H⁺) to H₂ in commercial electrolyzers, with a low overpotential (η), long durability, and high turnover frequency (TOF).³ However, Pt is a precious metal, partly due to its relative scarcity in the Earth's crust. Consequently, more earth-

abundant, heterogeneous electrocatalysts have been sought and reported, including metal chalcogenides,⁵⁻⁷ carbides,⁸ phosphides,⁹⁻¹¹ and hydroxides,^{12,13} in attempts to produce H₂ at prices competitive with the production from fossil fuels.

Concurrent with the research on heterogeneous catalysts, a number of molecular complexes consisting of earth-abundant elements have been found to be exceptional H₂ evolution electrocatalysts. These complexes display especially impressive TOFs in organic solvents, some of which surpass the activities of natural hydrogenase enzymes, and are supported by ligands including N₂P₂,¹⁴⁻¹⁷ macrocyclic oximes,¹⁸⁻²⁰ polypyridines,^{21,22} thiolates,²³⁻²⁶ and porphyrins.²⁷ A select few of the molecular electrocatalysts are active in aqueous media and ligated by scaffolds including PY5Me₂,²⁸ DPA-Bpy,²⁹ and P₄N₂.³⁰ Co salicylaldimine catalysts have also been used for photodriven H₂ evolution in water.³¹ Among the most active catalysts, a common feature has been the judicious customisation of the second coordination sphere *via* the introduction of bioinspired H⁺ relays. These complexes poise Lewis basic amine and Bronsted acidic alcohol groups in close proximity to the redox-active metal centre, similar to natural enzymatic systems. However, few studies have documented the effects of alkali metal ions in the second coordination sphere of molecular H₂ evolution electrocatalysts, although copious amounts of alkali metal cations are found in seawater and biological systems.

Herein, we describe the H₂ evolution activity of new nickel (Ni) complexes supported by salicylaldimine ligands with pendant, chelating ether groups that can bind Lewis acids such as alkali metal cations. The alkali metal ion-binding capabilities of salen-type ligands without pendant ether functionalities have been previously observed in molecular CO₂ complexes.³² The role of alkali metal cations is important since they constitute the most practical and cheapest electrolytes, and will be especially relevant if seawater (Na⁺) is to become the ultimate aqueous medium for large-scale H⁺ reduction.

We demonstrate that our water-soluble Ni electrocatalysts, which are readily accessible in a few steps from commercially available chemicals (Scheme 1), behave as H₂ evolution catalysts under both *neutral* and acidic aqueous solutions.

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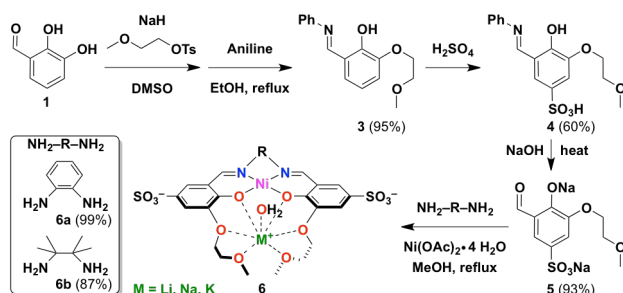
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Electronic Supplementary Information (ESI) available: Detailed synthetic procedures and characterisation, additional electrochemistry data, XPS results, TEM, and DLS data are included. CCDC 1435734-1435735. For ESI and crystallographic data in CIF or other electronic formats, see DOI: 10.1039/c000000x/

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Moreover, the chelating methoxyethoxy can bind hydrated alkali metal cations to provide hydrogen-bonding stabilisation and enhanced electrocatalytic proton reduction reactivity.



Scheme 1. Synthesis of Ni catalysts (**6**) with pendant ether groups.

The ligands were prepared by adaptations of previously reported methods.^{33–35} Compound **3** and subsequent organic molecules and Ni complexes are new and their syntheses and characterisation are included in the Electronic Supplementary information (ESI). The Ni complexes (**6**) were prepared by condensation of aldehyde **5**, a diamine, and nickel acetate with high yields (Scheme 1). Two design elements were introduced to enhance H₂ evolution from saline aqueous media: (i) introduction of sulfonate groups to improve water solubility; (ii) attachment of pendant, non-coordinating ether functionalities as hard Lewis bases for alkali metal cations. The salicylaldimine framework is highly modular and synthetically accessible; the amine and the aldehyde can be independently optimised and derivatised. Two distinct complexes **6** (diamine = *o*-phenylenediamine, **6a**; diamine = 2,3-dimethylbutane-2,3-diamine, **6b**) were prepared to compare their activities.

Both complexes have been characterised by NMR spectroscopy, high-resolution mass spectrometry, and elemental analyses. The deep orange **6a** displays bands at 262, 312, 360, and 486 nm ($\epsilon = 2.48 \times 10^4$, 1.03×10^4 , 1.19×10^4 and $3.13 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ respectively, Figure S1), which have been used to gauge **6a**'s stability under catalytic conditions (*vide infra*). Complex **6b** functions similarly as **6a**, with lower electrocatalytic activity. All subsequent studies have thus been performed with **6a**. Although we have not been able to grow single crystals of **6a** or **6b**, we were able to prepare **6c**, which has the same structure as **6a** without the sulfonate groups. Unlike numerous dimeric or polymeric Ni salen complexes,³³ **6c** is mononuclear (Figure S2).³⁶ The salient structural parameters are listed in Tables S1–S10. The coordination geometry around Ni is square planar, in accord with the d^8 electronic configuration. Notably, the pendant ether arms cradle one K⁺ cation similar to previous reports with Na⁺ (other examples in ESI),³⁶ potentially directing solvent molecules in close proximity to the Ni centre. Although this only represents the solid-state structure, UV-vis (Figure S3) and electrochemical experiments suggest that the alkali metal cations indeed influence the second coordination sphere around Ni in water during H₂ evolution catalysis (Scheme S1).

The cyclic voltammogram (CV, Figure S4) of **6a** in *N,N*-dimethylformamide (DMF) features a quasi-reversible redox couple at -1.04 V vs. NHE assigned to a metal-based Ni^{II}/Ni^I redox couple. The redox wave becomes increasingly reversible

at scan rates up to 1.0 V s^{-1} , which may be due to structural reorganisation or precipitation of the triply anionic transient species on the electrode.^{37, 38} In the presence of acetic acid (HOAc) as a weak proton donor in DMF, the CVs show moderate current increases with little change to the onset current (Figure S5), indicating that **6a** behaves as an electrocatalyst for H₂ evolution even with weak acids. When the stronger trifluoroacetic acid (TFA) was used as the proton source, the CV displayed a dramatic increase in the catalytic current over the background (Figure 1a), with an anodic shift of the onset current. After varying the concentration of TFA added, the CVs reveal a 2nd order dependence on the acid concentration (Figure S6).¹⁴ Attempts to perform a foot-of-the-wave analysis³⁹ on H₂ evolution in the presence of TFA have been complicated by significant deviations from linearity due to the anodic onset shift at higher TFA concentrations (Figure S7). This onset shift could be due to equilibrium protonation of the phenoxide donor at high acid concentrations (ESI),⁴⁰ which reduces the overpotential required for electrocatalytic H₂ evolution by positioning protons in close proximity to the Ni centre. Instead, foot-of-the-wave analysis using acetic acid as the proton donor demonstrates the expected linear behaviour, yielding an apparent rate constant of $17.9 \text{ M}^{-1} \text{ s}^{-1}$ in 0.10 M acetic acid at a scan rate of 100 mV s^{-1} (Figure S8).

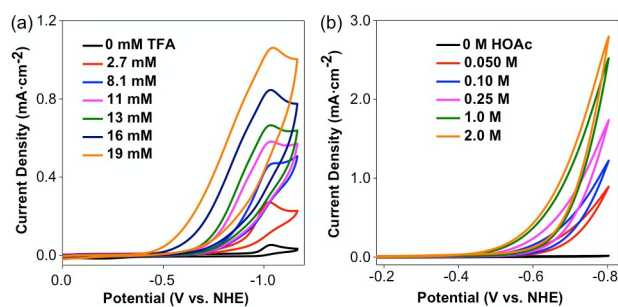


Figure 1. CVs of (a) 1.0 mM of **6a** in 0.10 M *n*-Bu₄NPF₆ in DMF with different concentrations of TFA; (b) 1.0 mM **6a** in 0.10 M Na₂SO₄ with different HOAc concentrations at scan rates of 100 mV s^{-1} with a glassy carbon working electrode (3 mm diameter).

Interestingly, the CV of **6a** in neutral water with Na₂SO₄ as the electrolyte exhibits a remarkable increase in the catalytic current at an onset of -1.05 V vs. NHE , corresponding to an overpotential of 0.59 V.† Gas bubbles are also observed during cathodic scans. The overpotential of **6a** is comparable to or lower than other molecular electrocatalysts that contain first-row transition metals and function in neutral water with glassy carbon working electrodes.⁴¹ For instance, the overpotentials for Co complexes ligated by P₄N₂ ligands³⁰ or DPA-Bpy₂²⁹ are about 0.55 and 0.78 V respectively, with glassy carbon working electrodes. When 0.10 M aqueous acetic acid is used (pH = 2.8), the catalytic onset shifts to -0.64 V , which is larger than the expected Nernstian shift of about 0.24 V due to an increase in [H⁺] by about four orders of magnitude (Figure 1b). In addition, the catalytic current shows a 1st order dependence on the concentration of **6a** (Figure 2a), suggesting that H₂ evolution occurs *via* protonation of a mononuclear Ni intermediate, rather than bimolecular coupling of two highly anionic Ni complexes (Scheme S1).⁴²

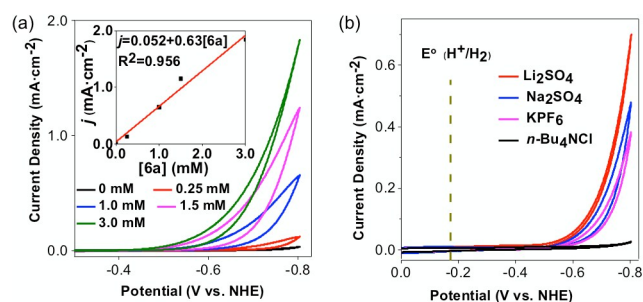


Figure 2. CVs of (a) different concentrations of **6a** complex in 0.10 M Na₂SO₄, 0.10 M HOAc solution; Inset: Linear relationship between current density *j* and [6a] at -0.80 V; (b) 1.0 mM **6a** in 0.10 M of different electrolytes in 0.10 M HOAc at scan rates of 100 mV s⁻¹ with a glassy carbon electrode (3 mm diameter).

To explore the effects of the pendant ether on **6a**, CVs have been conducted in the presence of *n*-Bu₄NCl, Li₂SO₄, Na₂SO₄, and KPF₆ as the electrolytes in 0.10 M acetic acid (Figure 2b). With *n*-Bu₄N⁺ as the electrolyte, the current density increases 0.70 mA·cm⁻² above the background current at an overpotential of 0.84 V in electrolyte solution with no added acids (Figure S9d). This indicates an appreciable, but slow H₂ evolution reaction. The *n*-Bu₄N⁺ cation is bulky and may hinder access to the Ni catalytic centre by hydronium ions, similar to the proton-gated hangman iron porphyrins reported by Nocera *et al.*⁴³ In contrast, with Na₂SO₄ as the electrolyte, the current density is 8.2 times compared to the catalytic current with *n*-Bu₄N⁺ as electrolyte (Figure S9). We observe the highest electrocatalytic current with Li⁺ as the electrolyte (11 times compared to *n*-Bu₄N⁺ as electrolyte, Figure S9) among the common and affordable cations examined. This dramatic increase in catalytic current highlights the non-innocence of the electrolyte in our H₂ evolution system, and emphasises the need for prudent management of second sphere effects around the catalytic centre (Scheme S1).⁴⁴⁻⁴⁶ In 0.10 M acetic acid, the electrocatalytic current increase also followed the same trend (Figure S10). The most Lewis acidic Li⁺ corresponds to the fastest catalytic behaviour. The Li⁺ with the highest charge density could more effectively introduce rigidity to the ether arms and direct H⁺ to the Ni centre, or electrostatically reduce the overpotential via inductive effects. Since seawater contains copious amounts of Na⁺ ions, judicious selection of pendant chelating groups that (size)-select for Na⁺ may prove fruitful in improving the catalytic performance of **6a** and are being explored.

In order to probe whether a heterogeneous catalyst is the major contributor of the H₂ evolution electrocatalysis, a series of standard electrochemical and spectroscopic experiments have been performed. The UV-vis, high-resolution mass, and ¹H NMR spectra (Figure S11-13) before and after controlled potential electrolysis (CPE) indicate that **6a** remains intact in solution, although there may be some adsorption. There were no nanoparticles observed by dynamic light scattering (DLS) measurements in the electrolyte solution after CPE for 2.5 h (Figure S14). The UV-vis spectra in Figure S10 show that the concentration of **6a** decreased to 90% and 78% after 1 h and 2.5 h, respectively.[†] We suspected that part of **6a** was

adsorbed on the carbon paper during the electrolysis process. To verify this conjecture, the used carbon paper electrodes in a CPE measurement were rinsed thoroughly with water before being subjected to CPE again (Figure S15). The used electrode showed a small, but non-negligible amount of catalytic activity. X-ray photoelectron spectroscopy (XPS) experiments were conducted on **6a** and the used carbon paper electrode after CPE (Figures S16-17). The data indicate that the small amounts of deposited material on the electrode have almost identical composition as **6a**, based on the XPS energies (Figure S16 and Table S11). We propose that some of the highly anionic **6a** is deposited on the carbon paper electrode upon reduction during catalysis, and cannot be readily rinsed off. A transmission electron microscopy (TEM) image (Figure S18) of the solution after CPE also exhibits little evidence of nanoparticle formation. Majority of the H₂ evolution electrocatalysis is still attributed to **6a** in homogeneous solution instead of deposited or suspended nanoparticles. Controlled potential electrolysis (CPE) experiments with a mercury pool electrode have been conducted to confirm the identity of the product by gas chromatography and gauge the stability of **6a** under catalytic conditions. The CPE measurements were performed in seawater obtained off the coast of Singapore (details in the ESI) with a mercury pool working electrode and a carbon rod counter electrode, at an overpotential of 0.84 V. As shown in Figure 3a, the amount of H₂ produced increased dramatically with a TON of 6.6 mol H₂

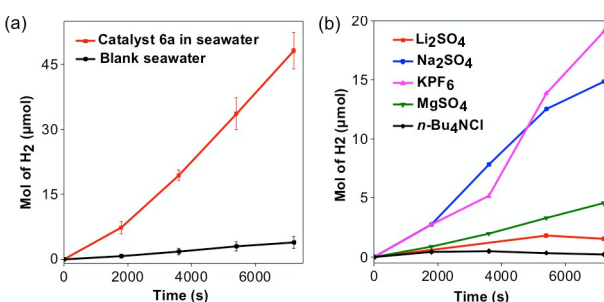


Figure 3. The amount of H₂ evolved from (a) seawater with 0.22 mM catalyst **6a** (red line) and only seawater (black line); (b) 0.10 M HOAc solution with 0.25 M Li₂SO₄ (red), Na₂SO₄ (blue), and Mg₂SO₄ (green), and 0.5 M KPF₆ (magenta) and *n*-Bu₄NCl (black) with catalyst **6a** using a mercury pool working electrode.

mol⁻¹ catalyst cm⁻² after 2 h, suggesting that **6a** is indeed suitable as a H₂ evolution catalyst with seawater as the medium. However, the Faradaic efficiency of H₂ production in seawater is only around 82%, since we have a one-compartment cell and some of the O₂ produced at the anode will be reduced at the cathode (Figure S19). To explore the effect of the cations in the electrolyte, CPE was also conducted with *n*-Bu₄NCl, Li₂SO₄, Na₂SO₄, KPF₆, and MgSO₄ as the electrolytes in 0.10 M acetic acid solutions (Figure 3b). The TON with KPF₆ as the electrolyte was the highest in these experiments (Table S12). We propose that the poor solubility of our Li and Mg complexes led to catalyst precipitation and amalgamation into the mercury pool electrode during CPE, which resulted in a discrepancy with the CV and CPE data that we collected using carbon-based electrodes. Nonetheless,

these CPE measurements and the TON and TOF (Table S12) confirm that **6a** remains active for electrocatalytic H⁺ reduction under almost neutral, saline aqueous conditions containing Na⁺ or K⁺, even when mercury electrodes are used to suppress the activity of nanomaterials.

Conclusions

We have prepared new mononuclear Ni complexes with salicylaldimine ligands that can be used as electrocatalysts for the production of H₂ in both neutral and acidic aqueous solutions. The chelating ether groups in the structure can bind alkali metal cations to form Lewis acids and promote the H⁺ reduction efficiency. Future studies will focus on modification of the Ni complexes with electron withdrawing substituents to reduce the overpotential, applying **6a** in photocatalytic units for H₂ evolution, and grafting the molecules on semiconductors for artificial photosynthesis.^{47, 48}

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Notes and references

† The onset overpotential is defined as the difference between the reversible potential of the H⁺/H₂ redox couple of neutral DI water (-0.46 V vs. NHE at pH 7.6) and the potential at which 10% of the current value at the peak potential was reached.

‡ The charge passed during CPE were 38 and 94 C at 1 and 2.5 h respectively, in excess of the charge needed to reduce Ni²⁺ to Ni⁰ (0.12 and 0.26 C for 10% and 22% **6a** respectively).

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