

Decreasing operating potential for water electrolysis to hydrogen *via* local confinement of iron-based soft coordination suprapolymers†

Cite this: *Phys. Chem. Chem. Phys.*, 2013, **15**, 15912

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Received 26th July 2013,
Accepted 26th July 2013

DOI: 10.1039/c3cp53152j

www.rsc.org/pccp

Currently there is intense interest in decreasing the operating potential for hydrogen evolution in water electrolysis to considerably decrease the energy cost. In this work we report a significant decrease of the operating potential for hydrogen evolution from neutral water mediated by an iron based soft coordination polymer (Fe^{III}-SCSP). The creation of a local acidic environment with a thickness in the range of ~40 nm on the surface of a glassy carbon electrode allows enrichment of H⁺ on the GCE, so that the operating potentials were effectively decreased. This strategy thus generates a new paradigm for lowering the operating potential of hydrogen generation from neutral water without the use of additional acids and organic cosolvents.

Introduction

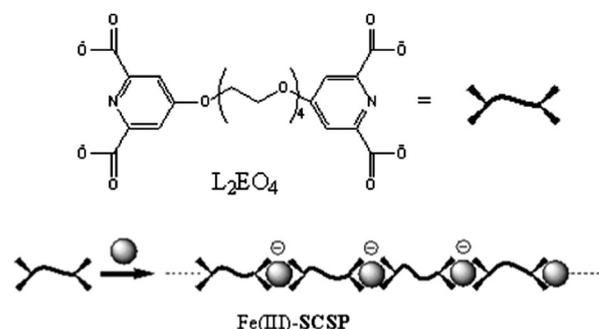
The electro-catalytic hydrogen production from water is a convenient way for renewable and sustainable energy storage.^{1,2} The cost of hydrogen production from water electrolysis is largely determined by the electrical energy expended, which is in turn governed by the operating voltage. For the purpose of decreasing the high proton reduction overpotential, various expensive catalysts for hydrogen evolution reaction (HER) are studied, such as platinum and platinum alloys,^{3–6} as well as the equally expensive iridium oxide (IrO₂) and ruthenium oxide (RuO₂) catalysts.⁷ However, the tremendous costs associated with the use of noble metal oxides have almost counterbalanced their contribution to lowering the operating voltage. In order to lower the cost triggered by the use of noble metals, molecular catalysts of the metal complexes made from Earth-abundant metals such as cobalt, nickel, iron or molybdenum have attracted wide attention.^{8–17} Although quite a few molecular catalysts are proved to decrease the operating potential effectively, organic acids, bases, additives or solvents are still required, which led to environmental problems.^{18–22} Therefore, the creation of Earth-abundant molecular systems that produce H₂ from neutral water with catalytic activity remains a significant basic science challenge.²³

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3cp53152j

In this work we report a unique film catalyst for H₂ production from neutral water using an iron-based reversible soft coordination suprapolymer (Fe^{III}-SCSP). The Fe^{III}-SCSP was formed by simply mixing Fe³⁺ solution and an aqueous solution of a ditopic ligand, pyridine-2,6-dicarboxylic acid (L₂EO₄, Scheme 1), in a 1 : 1 ratio, as described in our previous work.^{24–26} Each coordinating center carries one negative elementary charge. Because of the reversible coordination bonds between the metal centers and the ligands, they exhibit a concentration dependent polymerization degree.²⁶ In our previous work, it was found that the Fe^{III}-SCSP may lower the half-wave potentials for electrochemical reactions, meanwhile increasing the current upon being modified onto a glassy carbon electrode (GCE).²⁷ However, this occurs only in cases where the films are fully covered with over 6 pairs of modified layers, and the mechanism for this dual catalytic



Scheme 1 Structure of the water-soluble bifunctional ligand L₂EO₄ and the formation of soft coordination supramolecular polymers Fe³⁺-L₂EO₄ (Fe-SCSP) in water. Each coordination center carries one negative elementary charge.

performance was attributed to decrease of the overpotentials. In this work, we report that the Fe^{III} -SCSPs catalyze water electrolysis probably *via* a nanopool mechanism, which is different from our previous recognition. We found that considerable decrease of operating potential and increase of current (density) occurred even on the electrode modified with only one pair of the film, where the surface of the electrode was not fully covered. This was attributed to the generation of a local low pH environment on the modified GCE owing to the binding of OH to the iron centers. In the following we report the results in detail.

Experimental

Materials

The water soluble $\text{Fe}(\text{III})$ -SCSPs were prepared by simply mixing the aqueous solution of bisligand L_2EO_4 (Scheme 1) and fresh FeCl_3 solution in an equimolar ratio. $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$ and KNO_3 were purchased from Sigma-Aldrich. Polyethylenimine, branched, (PEI) was purchased from Aldrich with a M_w of 25 000. Milli-Q water was used when required.

Electrode modification

For the modification of electrodes used in this study, alternatively dropping 10 μl of aqueous solutions of PEI and $\text{Fe}(\text{III})$ - L_2EO_4 coordination polymers on the GCE or FTOE (to verify the success of the layer-by-layer assembly, Fig. S2a, ESI[†]) was adapted. Both solutions contain 0.1 M KNO_3 , which is the supporting electrolyte for electrochemical experiments. Prior to assembly, the GCE (0.07 cm^2) was first polished with a 0.05 mm alumina slurry by a polisher and then washed in H_2O and ethanol for 3 minutes by an ultrasonic cleaner. An FTO glass slide was sonicated in the mixed solvent of Lysol and Milli-Q water (volume ratio 1 : 3), and then sonicated 3 times in Milli-Q water each for another 30 minutes before use. PEI was deposited as the first layer on both the GCE and FTO glass electrodes. Then the surface was washed with Milli-Q water three times each for 1 min and dried under argon. Next, alternative assembling of Fe^{III} - L_2EO_4 coordination suprapolymers and PEI was carried out. The concentration of Fe^{III} - L_2EO_4 and PEI is 2 mM and 10 mM, and the assembling time is 15 and 1 minute, respectively. Then the films were rinsed with clean water before being dried under argon.

Electrochemical measurements

A CHI660C electrochemical workstation (Shanghai Chenhua Equipments, China) with a conventional three-electrode system was used to perform electrochemical measurements. A platinum wire was used as the counter electrode, and Ag/AgCl (3 mol L^{-1} KCl-filled) as the reference electrode. The scan rate for CV analysis was 100 mV s^{-1} . The modified (PEI/ Fe^{III} - L_2EO_4) $_n$ GCEs (0.07 cm^2) with various bilayer numbers n ($n = 1, 4, 6, 8$) as described before were fabricated and were used as working electrodes, and voltammetry measurements were conducted in 0.1 M KNO_3 solution.

Ultraviolet-visible (UV-vis) spectra

UV spectra of the aqueous solutions of L_2EO_4 , FeCl_3 and coordination complexes of $\text{Fe}(\text{III})$ - L_2EO_4 were collected on a Pgeneral TU-1810 UV-vis spectrophotometer.

X-ray photoelectron spectroscopy (XPS)

XPS measurements were carried out on an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al $K\alpha$ radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. Target PIC micelle solutions were dropped onto a clean silicon wafer, followed by drying naturally. To compensate for surface charge effects, binding energies were calibrated using the C 1s hydrocarbon peak at 284.80 eV. The data were converted into a VAMAS file format and imported into CasaXPS software package for manipulation and curve-fitting. Zeta potentials were measured using a temperature-controlled ZetaPALS zeta potential analyzer (Brookhaven Instruments Corporation).

Results and discussion

Electrochemical measurements for water hydrolysis were performed at $\sim 25^\circ\text{C}$ in a three-electrode cell connected to a CHI Instrument. A glassy-carbon electrode (GCE, 0.07 cm^2) coated with the $[\text{PEI}/\text{Fe}^{\text{III}}\text{-SCSP}]_n$ films was used as the working electrode whereas Ag/AgCl (3 mol L^{-1} KCl-filled) and a platinum wire served as the reference and counter electrodes, respectively. A 0.1 M KNO_3 solution was the electrolyte in the electrochemical measurements. The detailed procedures to prepare the Fe^{III} -SCSP and the Fe^{III} -SCSP modified GCE can be found elsewhere.²⁷ Succinctly speaking, 10 μl of the 1 : 1 mixed Fe^{3+} and L_2EO_4 aqueous solution and a PEI solution were alternatively dropped onto the GCE for assembling for 15 and 1 minute, respectively. The electrode was washed with Milli-Q water and allowed to dry under an argon atmosphere before assembling the next layer.

Fig. 1 shows the linear sweep voltammetry curves of the freshly prepared GCEs modified with $[\text{PEI}/\text{Fe}^{\text{III}}\text{-SCSP}]_n$ films with n in the range of 0–8. It is very striking that the onset

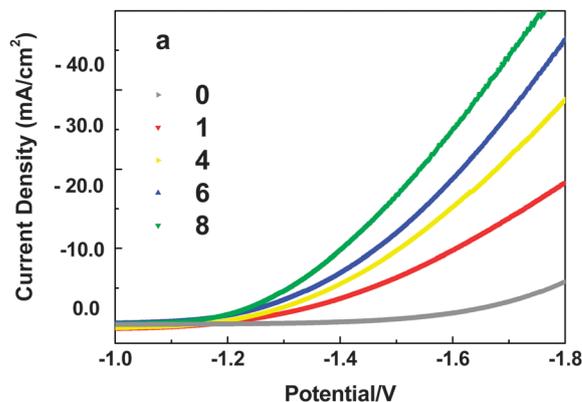


Fig. 1 Linear sweep voltammetry curves of H^+ reduction at the (PEI/ Fe^{III} -SCSP) $_n$ modified GCE surface. The area of the GCE is 0.07 cm^2 , n is the number of PEI/ Fe^{III} -SCSP pairs modified onto the GCE. Oxygen was removed before voltammetry measurements by purging with argon. Measurements were made vs. Ag/AgCl .

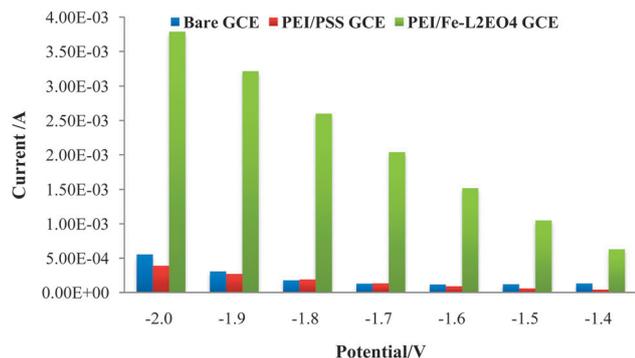


Fig. 2 Comparison of the currents on different GCEs operating at various potentials. Blue: bare GCE; red: GCE modified with 8 pairs of PEI/PSS, where PSS represents polystyrene sulphite, sodium salt; green: GCE modified 8 pairs of PEI/Fe^{III}-L₂EO₄.

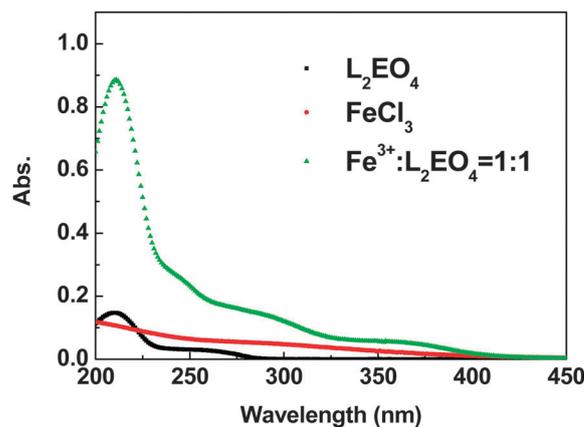


Fig. 3 UV spectra of the aqueous solutions of L₂EO₄, FeCl₃ and the coordination complex Fe-L₂EO₄.

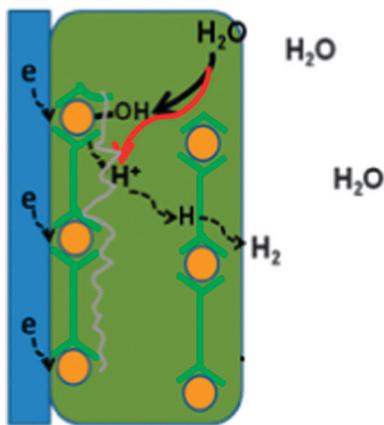
potential of proton reduction starts to shift to a more positive value even at $n = 1$, which is obviously different from our previous observations where catalytic behaviors for electroactive molecules can be observed only at n beyond 5.²⁷ It is demonstrated in Fig. 1 that on the bare GCE ($n = 0$), the onset potential is about -1.8 V, yet it has been decreased to -1.2 V on the 8 pair modified GCE. Although the absolute operating potentials in the literature for water electrolysis are not comparable due to the use of different working and standard electrodes,^{28–30} the 0.6 V drop in the operating potential is very significant, which is among the most efficient potential drop reported in the literature.^{21,22,28,29}

In line with the significant drop in operating potentials, the [PEI/Fe^{III}-SCSP]_{*n*} films give rise to sharp rises in current, indicating that a catalytic process occurred for water activation.^{21,28,31} In Fig. 2 we show the comparison of currents on the bare and the [PEI/Fe^{III}-L₂EO₄]₈ modified GCEs at different operating potentials. It can be clearly seen that dramatic enhancement of the current (density) can be achieved on the modified GCE in the range of -1.4 to -2.0 V. It is worth noting that at an operating potential of -1.5 V, the actual current has reached 1.2 mA, which is higher than the result obtained by Long *et al.* by 0.4 mA.²¹ and is comparable to that acquired on noble metals.^{32,33} In Long and Chang's study, a molecular molybdenum-oxo catalyst may produce a current of 0.8 mA in the process of water splitting on the GCE of the same size in acetic acid operating at 1.5 V.²¹ Since the Fe^{III}-SCSPs used in our study, though assembled into the films, are fully accessible to water, they are promising new molecular catalysts in electrochemical generation of hydrogen from neutral water.

To verify that the Fe^{III}-SCSPs are crucial for this catalytic hydrogen evolution to occur, we conducted the control experiments in which the negatively charged Fe^{III}-SCSP was replaced by a non-electrochemical active covalent polyelectrolyte, polystyrene sodium sulphite (PSS). In this situation, the electrode is not covered with electro-active species. As expected, we observed only decreases of the proton reduction current without a change in potential (Fig. S1, ESI[†]). This is the typical characteristic of the resistance effect of permissive non-conductive films, as reported by Bruening and Harris.³⁴

It is worth noting that the catalytic effect occurs even in the presence of only 1 pair of film, a situation where the GCE surface is not fully covered.²⁷ This indicates that the coordination polymer Fe^{III}-SCSP must have been involved in H₂ evolution. We expect that this is related to binding of the OH⁻ group to the iron centre which leads to the release of H⁺. This produces a local environment in the modified film that is rich in H⁺ which can be inferred from the pH of bulk Fe^{III}-SCSP aqueous solution. For a solution of 0.1 mM Fe^{III}-SCSP, the pH was found to be 3.5. Obviously, considerable protons are produced in the coordinating system, which is an indication of strong binding of OH⁻ to the central Fe³⁺ ion. This was further proved by the changes in UV measurements. In Fig. 3 we show the comparison of UV spectra of the aqueous solutions of Fe³⁺, L₂EO₄, and coordinating complexes of Fe^{III}-L₂EO₄. It is clear that Fe³⁺ ions exhibit featureless flat absorption resulting from various hydroxides Fe(OH)_{*n*}^{(*n*-3)⁻ in the range of 200–400 nm,³⁵ whereas the L₂EO₄ ligand shows no absorption beyond 300 nm. Upon coordination, strengthened absorption beyond 300 nm is observed. The flat feature of the absorption in this region is very similar to that observed in the Fe³⁺ aqueous solutions, and thus can be assigned to the contribution from the mixed coordination complex of Fe(OH)(L₂EO₄).³⁵ This species was indeed reported in the literature.^{35,36} Therefore, we can infer that this species may also exist in the film so that the pH in the films is about 3.5 which is much lower than that in the bulk. As a result, an acidic ‘nanopool’ was created on the modified GCE (Scheme 2). It has been estimated that the average thickness of the modified layer is about 4–5 nm per pair.³⁷ This means that the depth of the ‘nanopool’ is around 30–40 nm for an 8-pair modified electrode. The H⁺ in the ‘nanopool’ was reduced to the H atom which then forms H₂ (Scheme 2) upon applying a negative potential.}

Furthermore, X-ray Photoelectron Spectroscopy (XPS) measurements were conducted for the films after electrolysis of water for 10 minutes at -1.7 V to clarify whether Fe⁰ particles have been produced during the water splitting reaction. The XPS spectra in Fig. 4 show that the binding energy of the 2p electrons of iron is 710 eV and 723 eV, which is characteristic of



Scheme 2 Demonstration of the mechanism of H_2 evolution on the film of $\text{Fe}^{\text{III}}\text{-L}_2\text{EO}_4$ during the electrolysis.

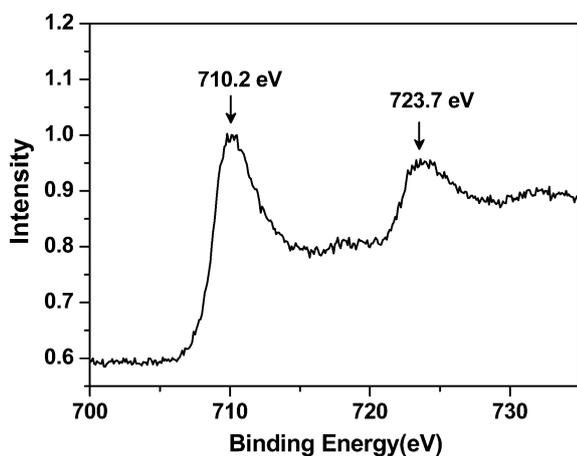


Fig. 4 Fe 2p XPS spectra of the $\text{Fe-L}_2\text{EO}_4$ films after electrolysis of water for 10 min at 1.7 V.

the presence of Fe^{II} .^{38–41} This means that in the presence of a strong coordination field, it is difficult to reduce Fe^{III} to Fe^0 . We have found that the reduced product of $\text{Fe}^{\text{III}}\text{-L}_2\text{EO}_4$ coordination complexes with the strong reducing agent NaBH_4 is $\text{Fe}^{\text{II}}\text{-L}_2\text{EO}_4$,⁴² which is in line with the results obtained in this study. On the basis of the above two experiments, we can unambiguously conclude that it is Fe-SCSP that catalyzed the water splitting.

It should be pointed out that the binding of OH to the Fe^{3+} center is reversible in the presence of L_2EO_4 . This can be verified by the changes in the solution pH of FeCl_3 before and after complexation with the L_2EO_4 ligand. The pH for the original Fe^{3+} solution is 2.4, while it increases to 3.5, suggesting that complexation between Fe^{3+} and L_2EO_4 is stronger than that between Fe^{3+} and OH . Therefore, the excess OH in the coordination sphere of Fe^{3+} will dissociate and is replaced by the chelating groups in L_2EO_4 . This reversible nature made the films enduring in the process of water electrolysis which is reflected in the long-term HER performance. In Fig. 5 we show the variation of current density under continuous electrolysis of the film on the GC electrode. Except for some potential drop caused by the accumulated H_2 bubbles on the film, the potential

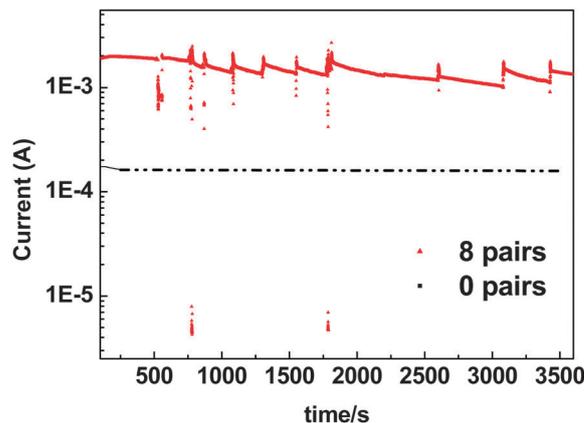


Fig. 5 Long time duration of current density of the films. The operating potential is -1.7 V. To avoid any experimental artifact from solvent evaporation and oxygen reduction, the long-term electro-chemical test cell was maintained under continuous water vapor-saturated N_2 purging.

readings from the electrochemical cell under continuous operation didn't decay significantly, suggesting good stability of the film. This indicates that the $\text{Fe}^{\text{III}}\text{-SCSP}$ films have application potentials in future HER studies.

Finally, in order to check whether uncomplexed Fe^{3+} ions or uncoordinated L_2EO_4 ligands have contributed to the catalytic performance, voltammetry measurements on the bare GCE against KNO_3 solutions containing the same amount of the above two species separately were conducted, and no catalytic effects were observed. Similarly, when the same amount of $\text{Fe}^{\text{III}}\text{-L}_2\text{EO}_4$ coordination complexes was dispersed in the same supporting electrolyte, no catalytic effect was observed as well, unambiguously verifying the necessity of the 'nanopool' in catalysis of hydrogen evolution.

In summary, we have reported an efficient hydrogen generation catalyst that works effectively when confined on the surface of an electrode *via* simple layer-by-layer assembly. It is possible that we have created an acidic 'nanopool' on the surface of an electrode and established a new paradigm in catalytic studies of hydrogen evolution *via* water electrolysis from neutral water without the use of additional acids and organic cosolvents. Ongoing efforts are focused on modifying the Fe-SCSP and related platforms to further facilitate sustainable energy cycles.

Acknowledgements

This work was supported by National Natural Science Foundation of China (NSFC, Grant No. 21173011, 20805002, and 21073006).

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