

Catalytic 'Gelectrodes' for Sustainable and Enhanced Oxygen Evolution Reaction

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KEYWORDS *Oxygen evolution reaction, Hydrogel, Nanocomposite*

ABSTRACT: Development of cost-effective catalysts that provide low overpotentials and enhanced electrochemical kinetics is a critical goal of contemporary research on electrochemical water splitting and similar technologically significant processes. Translation to practical applications demands that they should also enable high current densities to be extracted. A simple strategy of encapsulating the active electrocatalyst in hydrogel polymer matrices is shown to provide a solution in several respects, especially regarding the last criterion. The concept is illustrated using two examples of 'gelectrodes' based on nanocomposites of cobalt oxyhydroxide and nickel-iron hydroxide with chitosan on nickel foam, and their efficient mediation of the oxygen evolution reaction (OER). Comparison with various control systems show that significantly lower overpotentials and higher current densities with extended temporal stability can be achieved with the gelectrodes; the cobalt oxyhydroxide - chitosan and nickel-iron hydroxide - chitosan systems provide stable current densities up to 1.6 - 1.7 A cm⁻² for the OER with alkaline aqueous electrolyte. This simple design strategy is expected to open up a general route to technologically useful electrocatalyst performance.

Hydrogen has approximately thrice the energy content than gasoline, on a mass basis (120 MJ kg⁻¹ vs 44 MJ kg⁻¹).¹⁻³ The additional attraction of environmentally benign combustion product lends it the 'green' epithet, making it the choice fuel for future technologies. Among the various routes to hydrogen generation, electrocatalytic water splitting is one of the most promising.^{4,5} Some of the critical challenges in developing practically sustainable electrocatalytic water splitting technology are the high cost of efficient catalysts for the hydrogen evolution reaction (HER) and the multi-electron oxygen evolution reaction (OER), maintenance of the catalyst integrity and stability, and technical/design issues of scale up.⁶⁻⁸ Development of appropriate solutions must take into account (i) the use of non-noble metal based and easily synthesized electrocatalysts, (ii) fabrication of catalytic electrodes that ensure efficient protection of the catalyst in suitable matrices that prevent leaching while enabling facile access of the electrolyte and release of the reaction products, and (iii) potential scale-up and thermal/mechanical stability of the catalyst-matrix composites.^{9,10} Recent studies in our laboratory¹¹⁻¹⁴ have shown that the deployment of polymers that possess hydrogel characteristics opens up a wide gamut of options as the matrix to embed the selected electrocatalyst paving the way to address the challenges outlined above. Significant observations from various laboratories, of the critical role of superaerophobic surfaces in promoting HER^{15,16} and OER,¹⁷ and tuning the water states in supramolecular hydrogel electrolytes¹⁸ are pertinent in this context. Many of these efforts have in-

volved specialized hydrogels and elaborate fabrication processes.

Past and contemporary research aimed at enhancing the efficiency of the electrocatalysts for water splitting reactions have largely been focused on lowering the overpotentials for the HER and OER, enhancing their kinetics, and extending the stability of the catalytic electrodes.¹⁹⁻²² Use of hydrogel polymers for embedding the electrocatalysts have led to similar advantages,^{11,12,23} and the added benefits of the active role of the polymer matrix in enhancing the activity through optimized cycling protocols.^{13,14} However, in order to realize practically relevant electrocatalytic water splitting, significantly high and sustainable current densities need to be extracted at reasonably low overpotentials.^{24,25} We report a protocol that can easily be generalized, to embed or enclose established or novel, efficient and cost-effective catalysts in common and widely available hydrogel polymer matrices that leads to sustainable and enhanced electrocatalytic activity. As illustrative cases, we present our exploration of cobalt oxyhydroxide (CoOOH) and nickel-iron hydroxide (Ni_{1-x}Fe_x(OH)_y) encapsulated in polymers such as poly(acrylamide-co-acrylic acid) (PAM), polyacrylic acid (PAA), poly(2-hydroxyethyl methacrylate) (PHEMA) and chitosan (CS), and formed as thin films on Ni foam (NF); we call these 'gelectrodes'. The former is a CoOOH-polymer composite coated on NF, and the latter Ni_{1-x}Fe_x(OH)_y formed on the NF surface²⁶ and over-coated with the polymer. Our studies demonstrate efficient and sustainable OER with high current densities achieved

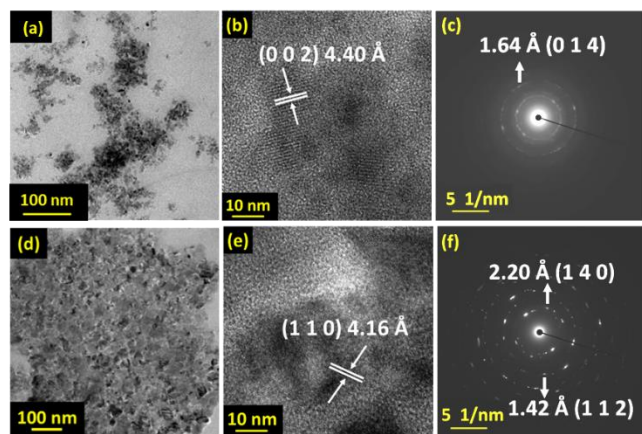


Figure 1. (a) TEM image (scale bar = 100 nm), (b) HR-TEM image showing the lattice plane spacing (scale bar = 10 nm), and (c) electron diffraction pattern of CoOOH-CS. (d-f) Corresponding images and diffraction pattern of $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y\text{-CS}$.

with CS as the matrix for the nanocomposite thin film. The overpotentials obtained with CoOOH-CS/NF and $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y\text{-CS/NF}$ are 311 mV and 275 mV @10 mA cm⁻² respectively; compared to the native catalyst on the same conducting substrate, substantially higher and stable current densities up to 1.7 A cm⁻² are attained.

CoOOH and $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y$ were synthesized following reported procedures.^{13,26,27} Trial experiments with various polymers led to the choice of chitosan (CS), that

provided the nanocomposite electrode capable of OER with the lowest overpotentials and stable, high current densities. The nanocomposite CoOOH-CS/NF was fabricated by simple mixing of CoOOH and CS in 1% acetic acid and drop-casting on NF. $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y\text{-CS/NF}$ was prepared by drop casting CS on $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y\text{/NF}$ and drying in air (Figures S1, S2, Table S1). The TEM images confirm the formation of CoOOH (Figure 1a-c; JCPDS: 96-900-9450) and $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y\text{-CS}$ (Figure 1d-f).²⁸ Core level XPS of CoOOH (Figure 2a) shows the presence of Co²⁺ and Co³⁺ and oxygen in the expected environments (Tables S2, S3, Figure S3). Core level XPS in Figure 2b,c show that Ni²⁺, Fe²⁺ and Fe³⁺ are present in ~ 0.53:0.23:0.24 atomic ratio in $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y\text{-CS}$,^{29,30} based on this, *x* and *y* can be estimated to be 0.47 and 2.24 respectively so that the material can be formulated as $\text{Ni}_{0.53}\text{Fe}_{0.47}(\text{OH})_{2.24}$.

CoOOH-polymer/NF and $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y\text{-polymer/NF}$ were used as the working anode in the electrochemical water splitting reaction in a standard 3-electrode configuration with Pt as the counter electrode and Hg/HgO as the reference electrode. Figure 3a shows the CV plots recorded for the OER at 10 mV s⁻¹ with CoOOH-polymer/NF (Figure S4 provides the corresponding polarization plots). The plots with the hydrogel polymers, poly-L-lysine, PAM, PAA, PHEMA and CS are shown; the catalytic electrode prepared with Nafion as the binder is included as the control. CoOOH-CS/NF is found to show the lowest overpotential of 311 mV @10 mA cm⁻². Experiments with selected cases of $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y\text{-polymer/NF}$ (with $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y\text{/NF}$ used as the control)

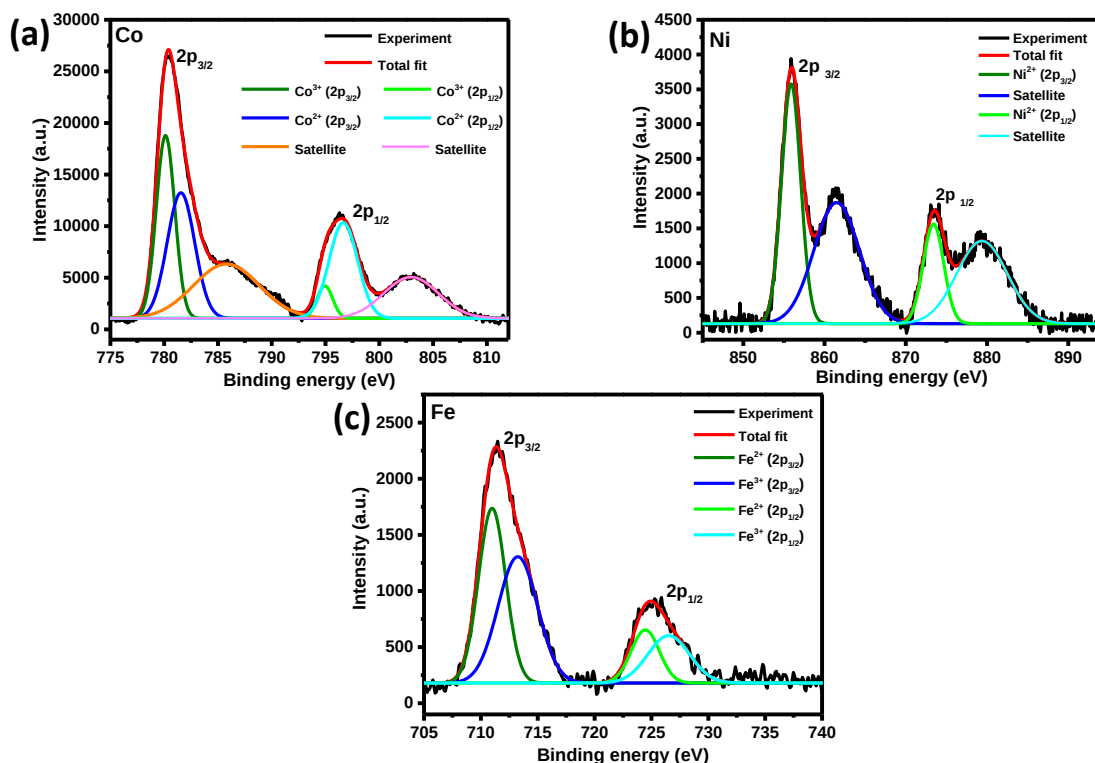


Figure 2. Core-level XPS of (a) CoOOH (Co) and (b, c) $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y\text{-CS/NF}$ (Ni, Fe) showing also the spectral deconvolutions; the experimental spectra (black line), the total fitting (red line), and individual components are shown.

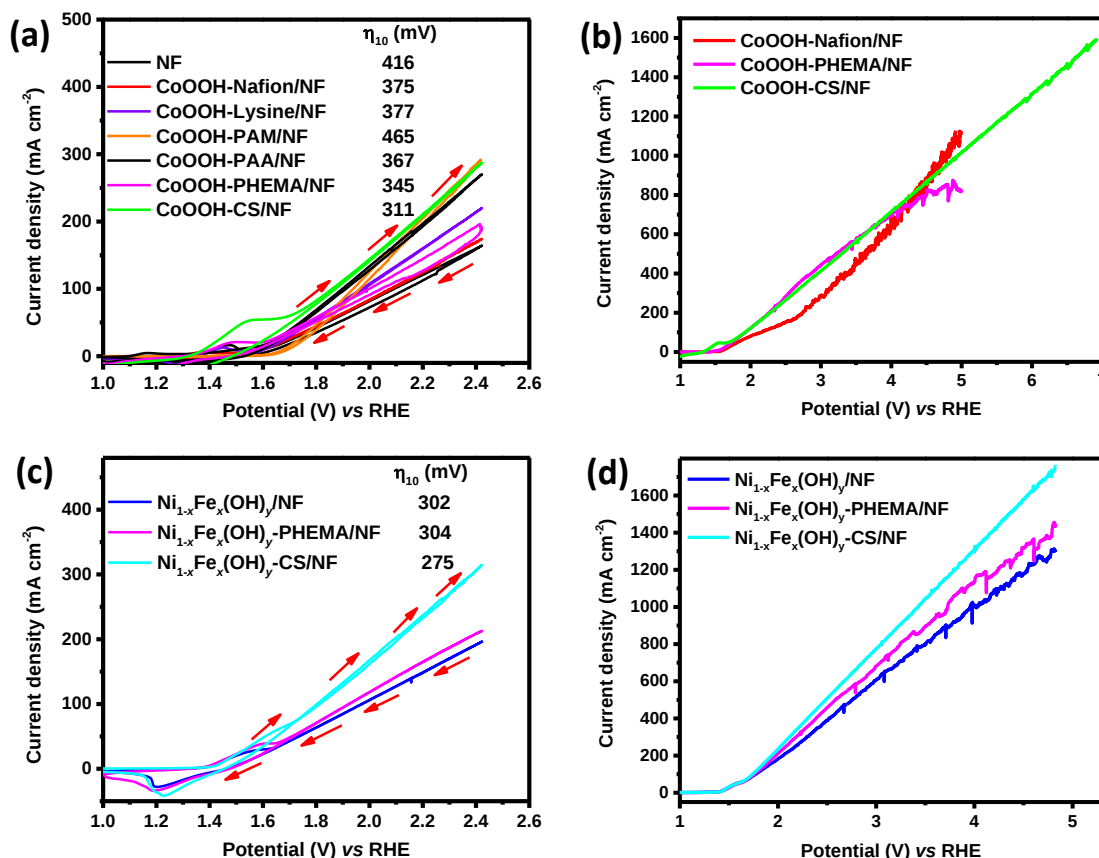


Figure 3. (a) CV plots for the OER using various CoOOH-polymer/NF (the overpotentials are estimated from the reverse sweep to avoid the oxidation peak, $\text{Ni}^{2+}/\text{Ni}^{3+}$), and (b) the polarization plots of selected cases recorded up to higher potentials. (c, d) Similar plots for OER using $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y$ -polymer/NF.

showed that the nanocomposite with CS again provides the lowest overpotential of 275 mV @10 mA cm^{-2} . The hydrogel polymer stabilizes the electrocatalyst; its swelling and confinement of the electrolyte within lead to the enhancement of the electrocatalytic efficiency. Figures 3b, d show that technologically relevant current densities up to $\sim 1.6 - 1.7 \text{ A cm}^{-2}$ can be obtained with the CS-based gelectrodes; the control systems show significant fluctuations or fail at much lower current densities. Beyond the low overpotentials and stable water splitting performance demonstrated in our earlier studies,¹¹⁻¹⁴ the current observations add a new dimension of realizing high current densities with the hydrogel based nanocomposite thin films.

The enhanced catalytic activity of the gelectrodes prepared with CS is also reflected in the Tafel plots of CoOOH-CS/NF and $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y$ -CS/NF (Figure 4a), the slopes of 96.9 and 77.0 mV dec^{-1} respectively being significantly lower than that of the control cases. We have also calculated the electrochemically active surface area (ECSA) by estimating the double layer capacitance (Figures 4b, S5). The ECSA values nearly quadruple from 7.65 cm^2 with CoOOH-Nafion/NF to 33.5 cm^2 with CoOOH-CS/NF; similarly, the value increases from 19.8 cm^2 with $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y$ /NF to 34.7 cm^2 with $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y$ -CS/NF (Table S5). Parallel trends are observed with the Faradaic efficiency, measured by volumetric analysis of the O_2 pro-

duced; high efficiencies of 97% and 87% are obtained with CoOOH-CS/NF and $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y$ -CS/NF respectively (Figures 4d, S6). The TOF for OER evaluated using Co and Fe content in the two electrodes (determined by ICP elemental analysis) are 16.2 and 25.4 h^{-1} respectively (pages S13, S14).²⁷ Encapsulation of the electrocatalyst within the hydrogel polymer improves the stability and efficiency of the working electrode, as illustrated by the chronoamperometry and chronopotentiometry plots in Figures 4d, e. The current density obtained at 3 V and the voltage required for 50 mA cm^{-2} show significant increase and decrease respectively, from CoOOH-Nafion/NF to CoOOH-CS/NF to $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y$ -CS/NF. The parallel enhancement of temporal stability demonstrated for 24 h, is clearly extendable to longer time periods. The high current densities that can be extracted over extended time periods using the gelectrodes are especially notable. Figure 5 shows the polarization plots for water splitting with 2-electrode cells having Pt as the cathode and CoOOH and $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y$ based gelectrodes as the anodes. The cell voltages required to achieve a current density of 100 mA cm^{-2} decrease from 2.124 V with CoOOH-Nafion/NF to 1.899 V with CoOOH-CS/NF, and from 1.968 V with $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y$ /NF to 1.892 V with $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_y$ -CS/NF. This clearly demonstrates the enhanced efficiency for the high current water splitting process using the gelectrodes.

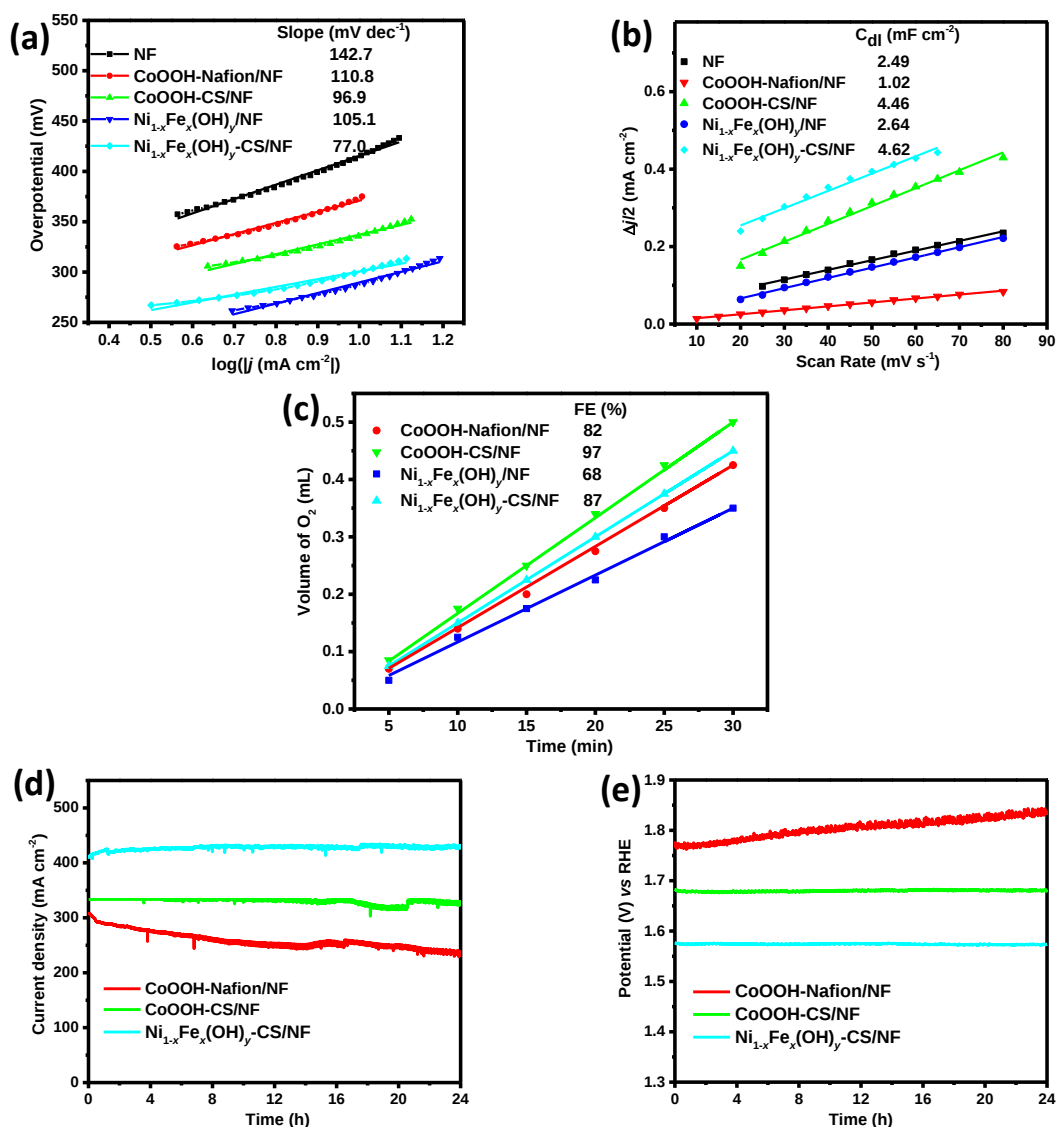


Figure 4. (a) Tafel plot for the different catalytic electrodes. (b) Plot of $\Delta j/2$ (Δj = anodic current density – cathodic current density) vs scan rate used to calculate the double layer capacitance. (c) Plot of the volume of O₂ produced by 5 mA current vs time, using different electrodes (the lines are based on the Faradaic efficiencies shown, calculated for the 30 min data point). Stability of the catalysts demonstrated using (d) chronoamperometry and (e) chronopotentiometry plots for the OER carried out at 3 V vs RHE, and 50 mA cm⁻² respectively using the CoOOH and Ni_{1-x}Fe_x(OH)_y based catalytic electrodes.

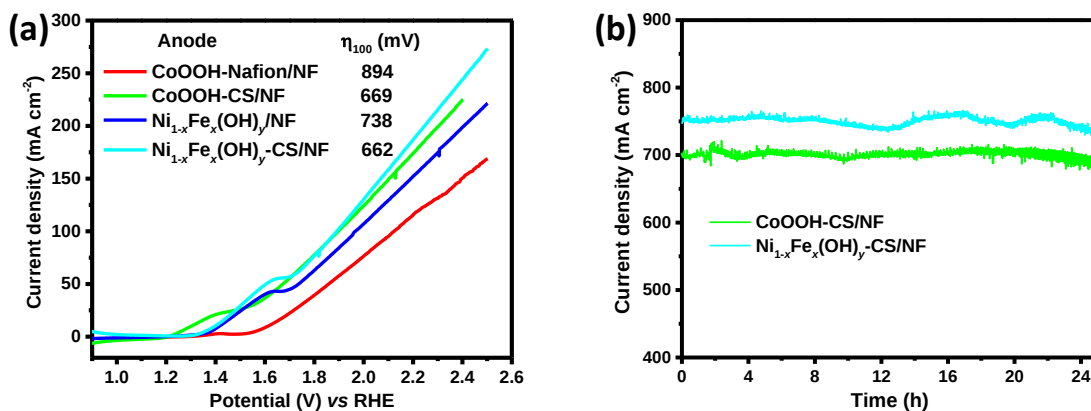


Figure 5. (a) Polarization plots recorded at a 10 mV s⁻¹ scan rate for the 2-electrode cell using the gelectrodes CoOOH-CS/NF and Ni_{1-x}Fe_x(OH)_y-CS/NF as the anode and Pt wire as the cathode; control experiments with CoOOH-Nafion/NF and Ni_{1-x}Fe_x(OH)_y/NF are also shown. (b) Chronoamperometry plots at an applied voltage of 4 V.

The hydrogel polymer matrix plays multiple roles in enhancing the capabilities of the electrocatalyst. It protects the nanocatalyst from leaching and potential chemical changes in the alkaline environment; confinement of the electrolyte promotes the charge transfer processes and hence the electrochemical kinetics. The aerophobic character facilitates efficient disposal of the gaseous products of the reaction supporting sustained high current flow. The present study thus demonstrates the low overpotentials, and more prominently, the high and stable current densities that can be extracted for electrocatalytic water splitting using the simple approach of encapsulating the active OER catalysts in hydrogel based polymers. The gelectrodes fabricated with the cheap and commercially available chitosan is shown to provide excellent performance (comparison with earlier reported systems is provided in Table S6) pointing to a cost-effective route to practically useful electrochemical water splitting. This general concept can be extended to other critical electrocatalytic processes using a wide range of options with a new generation of gelectrodes.

ASSOCIATED CONTENT

Details of synthesis, characterization, electrochemical experiments, and comparison with earlier reports (17 pages).

CONFLICT OF INTEREST

There are no conflicts to declare.

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FUNDING SOURCES

Financial support from the DST-SERB, New Delhi (File No. CRG/2021/000308), and infrastructure support from the School of Chemistry, University of Hyderabad (Institution of Eminence) are acknowledged with gratitude. AB thanks the Ministry of Education, Government of India, for the award of the Prime Minister's Research Fellowship (PMRF ID: 3700975).

REFERENCES

- Paik Suh, M.; Jeong Park, H.; Prasad, T. K.; Lim, D. Hydrogen Storage in Metal Organic Frameworks. *Chem. Rev.* **2012**, *112*, 782–835.
- Zhou, Z.; Pei, Z.; Wei, L.; Zhao, S.; Jian, X.; Chen, Y. Electrocatalytic Hydrogen Evolution Under Neutral pH Conditions: Current Understandings, Recent Advances, and Future Prospects. *Energy Environ. Sci.* **2020**, *13*, 3185–3206.
- Raveendran, A.; Chandran, M.; Dhanusuraman, R. A Comprehensive Review on the Electrochemical Parameters and Recent Material Development of Electrochemical Water Splitting Electrocatalysts. *RSC Adv.* **2023**, *13*, 3843–3876.
- Zou, X.; Zhang, Y. Noble Metal-Free Hydrogen Evolution Catalysts for Water Splitting. *Chem. Soc. Rev.* **2015**, *44*, 5148–5180.
- Yu, Z.; Duan, Y.; Feng, X. Y.; Yu, X.; Gao, M. R.; Yu, S. H. Clean and Affordable Hydrogen Fuel from Alkaline Water Splitting: Past, Recent Progress, and Future Prospects. *Adv. Mater.* **2021**, *33*, 2007100.
- Jiang, W.J.; Tang, T.; Tang, T.; Zhang, Y.; Hu, J. S. Synergistic Modulation of Non-Precious-Metal Electrocatalysts for Advanced Water Splitting. *Acc. Chem. Res.* **2020**, *53*, 1111–1123.
- Yao, D.; Gu, L.; Zuo, B.; Weng, S.; Deng, S.; Hao, W. A Strategy for Preparing High-Efficiency and Economical Catalytic Electrodes toward Overall Water Splitting. *Nanoscale* **2021**, *13*, 10624–10648.
- Sun, H.; Xu, X.; Kim, H.; Jung, W.; Zhou, W.; Shao, Z. Electrochemical Water Splitting: Bridging the Gaps Between Fundamental Research and Industrial Applications. *Energy Environ. Mater.* **2023**, *6*, e12441.
- Li, X.; Hao, X.; Abudula, A.; Guan, G. Nanostructured Catalysts for Electrochemical Water Splitting: Current State and Prospects. *J. Mater. Chem. A* **2016**, *4*, 11973–12000.
- Cao, J.; Ji, Y.; Shao, Z. Nanotechnologies in Ceramic Electrochemical Cells. *Chem. Soc. Rev.* **2024**, *53*, 450–501.
- Madhuri, U. D.; Radhakrishnan, T. P. Insulating Polymer-Hydrogel Nanocomposite Thin Film - Based Catalytic Electrode for Efficient Oxygen Evolution Reaction. *ChemElectroChem* **2019**, *6*, 1984–1989.
- Madhuri, U. D.; Radhakrishnan, T. P. In Situ-Fabricated Hydrogel Polymer - Semiconductor Nanocomposite Thin Film as a Highly Efficient and Robust Electrocatalyst for Hydrogen Evolution Reaction. *J. Phys. Chem. C* **2020**, *124*, 44–51.
- Dhanasekaran, T.; Bovas, A.; Radhakrishnan, T. P. Hydrogel Polymer-PBA Nanocomposite Thin Film-Based Bifunctional Catalytic Electrode for Water Splitting: The Unique Role of the Polymer Matrix in Enhancing the Electrocatalytic Efficiency. *ACS Appl. Mater. Interfaces* **2023**, *15*, 6687–6696.
- Bovas, A.; Dhanasekaran, T.; Pillai, K. V.; Radhakrishnan, T. P. An In Situ Fabricated Hydrogel Polymer – Palladium Nanocomposite Electrocatalyst for the HER: Critical Role of the Polymer in Realizing High Efficiency and Stability. *Chem. - A Eur. J.* **2023**, *29*, e202302593.
- Jeon, D.; Park, J.; Shin, C.; Kim, H.; Jang, J. W.; Lee, D. W.; Ryu, J. Superaerophobic Hydrogels for Enhanced Electrochemical and Photoelectrochemical Hydrogen Production. *Sci. Adv.* **2020**, *6*, eaaz3944.
- Kang, Y.; Lee, S.; Han, S.; Jeon, D.; Bae, M.; Choi, Y.; Lee, D. W.; Ryu, J. Versatile Stable and Scalable Gel-Like Aerophobic Surface System (GLASS) for Hydrogen Production. *Adv. Funct. Mater.* **2024**, *34*, 2308827.
- Xu, W.; Lu, Z.; Wan, P.; Kuang, Y.; Sun, X. High-Performance Water Electrolysis System with Double Nanostructured Superaerophobic Electrodes. *Small* **2016**, *12*, 2492–2498.

18. Li, C.; Zhu, X.; Wang, D.; Yang, S.; Zhang, R.; Li, P.; Fan, J.; Li, H.; Zhi, C. Fine Tuning Water States in Hydrogels for High Voltage Aqueous Batteries. *ACS Nano* **2024**, *18*, 3101-3114.
19. You, B.; Sun, Y. Innovative Strategies for Electrocatalytic Water Splitting. *Acc. Chem. Res.* **2018**, *51*, 1571-1580.
20. Wang, X.; Vasileff, A.; Jiao, Y.; Zheng, Y.; Qiao, S. Z. Electronic and Structural Engineering of Carbon-Based Metal-Free Electrocatalysts for Water Splitting. *Adv. Mater.* **2019**, *31*, 1803625
21. Yu, J.; Dai, Y.; He, Q.; Zhao, D.; Shao, Z.; Ni, M. A Mini-Review of Noble-Metal-free Electrocatalysts for Overall Water Splitting in Non-Alkaline Electrolytes. *Mater. Reports Energy* **2021**, *1*, 100024.
22. Mavric, A.; Cui, C. Advances and Challenges in Industrial-Scale Water Oxidation on Layered Double Hydroxides. *ACS Appl. Energy. Mater.* **2021**, *4*, 12032-12055.
23. Yang, j.; Wang, X.; Li, B.; Ma, L.; Shi, L.; Xiong, Y.; Xu, H. Novel Iron/Cobalt-Containing Polypyrrole Hydrogel-Derived Trifunctional Electrocatalyst for Self-Powered Overall Water Splitting. *Adv. Funct. Mater.* **2017**, *27*, 1606497.
24. Wang, C.; Zhu, M.; Cao, Z.; Zhu, P.; Cao, Y.; Xu, X.; Xu, C.; Yin, Z. Heterogeneous Bimetallic Sulfides Based Seawater Electrolysis towards Stable Industrial-Level Large Current Density. *Appl. Catal. B Environ.* **2021**, *291*, 120071.
25. Du, H.; Wang, T.; He, S.; Li, B.; Wang, K.; Chen, Q.; Du, Z.; Ai, W.; Huang, W. Mountain-Shaped Nickel Nanostripes Enabled by Facet Engineering of Nickel Foam: A New Platform for High-Current-Density Water Splitting. *Adv. Funct. Mater.* **2024**, *34*, 2311854.
26. Dong, G.; Fang, M.; Zhang, J.; Wei, R.; Shu, L.; Liang, X.; Yip, S.; Wang, F.; Guan, L.; Zheng, Z.; Ho, J. C. *In Situ* Formation of Highly Active Ni-Fe Based Oxygen-Evolving Electrocatalysts via Simple Reactive Dip-Coating. *J. Mater. Chem. A* **2017**, *5*, 11009-11015.
27. See Supporting Information for details.
28. Meng, C.; Lin, M.; Sun, X.; Chen, X.; Chen, X.; Du, X.; Zhou, Y. Laser Synthesis of Oxygen Vacancy-Modified CoOOH for Highly Efficient Oxygen Evolution. *Chem. Commun.* **2019**, *55*, 2904-2907.
29. Jiang, Q. S.; Li, W.; Wu, J.; Cheng, W.; Zhu, J.; Yan, Z.; Wang, X.; Ju, Y. Electrodeposited Cobalt and Nickel Selenides as High-Performance Electrocatalytic Materials for Dye-Sensitized Solar Cells. *J. Mater. Sci. Mater. Electron.* **2019**, *30*, 9429-9437.
30. Liu, C.; Zhu, H.; Zhang, Z.; Hao, J.; Wu, Y.; Guan, J.; Lu, S.; Duan, F.; Zhang, M.; Du, M. Binary Nickel Iron Phosphide Composites with Oxidized Surface Groups as Efficient Electrocatalysts for the Oxygen Evolution Reaction. *Sustain. Energy Fuels* **2019**, *3*, 3518-3524.

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