

# UC Berkeley

## UC Berkeley Previously Published Works

### Title

Reports From The Frontier: Overcoming Limitations for Pure-water Anion-exchange-membrane Electrolysis

### Permalink

<https://escholarship.org/uc/item/6vq0f4f1>

### Journal

The Electrochemical Society Interface, 32(2)

### ISSN

1064-8208

### Authors

Lindquist, Grace

Boettcher, Shannon

### Publication Date

2023-06-01

### DOI

10.1149/2.f05232if

Peer reviewed

FEATURED ARTICLES

## Reports From The Frontier: Overcoming Limitations for Pure-water Anion-exchange-membrane Electrolysis

To cite this article: Grace Lindquist and Shannon Boettcher 2023 *Electrochem. Soc. Interface* **32** 32

View the [article online](#) for updates and enhancements.

### You may also like

- [Effect of Carbonate Anions on the Stability of Quaternary Ammonium Groups for Aemfcs](#)  
Sapir Willdorf-Cohen, Songlin Li, Simcha Srebnik et al.
- [Mechanical and Physio-Chemical Properties of Anion Exchange Membranes and Their Implications on Industrial Scale Water Electrolysis](#)  
Andre Klinger, Guenter Schmid, Nemanja Martic et al.
- [\(Digital Presentation\) Nickel Iron Layered Double Hydroxide As a Promising Anode for AEM Water Electrolyzer Presenting High Performance and Durability](#)  
Irina Galkina, Wulyu Jiang, Alaa Y. Faid et al.

# Overcoming Limitations for Pure-water Anion-exchange-membrane Electrolysis

by Grace A. Lindquist and Shannon W. Boettcher

**M**any essential industrial processes rely on the input of high-purity H<sub>2</sub>, such as fertilizer and steel production.<sup>1</sup> However, over 99% of H<sub>2</sub> is “gray” (produced using fossil fuels).<sup>2,3</sup> Less than 1% is “green” H<sub>2</sub>, produced through water electrolysis powered by renewable electricity.<sup>2</sup> While gray H<sub>2</sub> is currently cheaper to produce, green H<sub>2</sub> is expected to become cost-competitive within the next decade as electricity costs decrease and device scale increases.<sup>1</sup> Electrolyzer technology also addresses long-duration energy-storage limitations facing scaling renewable electricity sources like wind and solar.<sup>4</sup> Pairing these systems with electrolysis stores excess energy as H<sub>2</sub>, which can be compressed for long-term storage or transport.

The two dominant commercial low-temperature electrolysis technologies are liquid-alkaline and proton-exchange-membrane (PEM) electrolysis.<sup>5</sup> Liquid-alkaline electrolyzers are a mature technology that operate by flowing hot, concentrated aqueous KOH to the anode and cathode separated by a porous diaphragm. They use inexpensive non-platinum-group-metal (non-PGM) catalysts and hardware but historically suffer from high crossover rates, resulting in O<sub>2</sub> contamination in the H<sub>2</sub> stream, which can be highly combustible. This approach is particularly ill-suited for pairing with renewable technology due to the inherent variability of the power load.<sup>6</sup> PEM electrolyzers operate using a cation-selective, solid-polymer membrane which reduces gas crossover, resulting in high-purity H<sub>2</sub> output and enabling the variable-load operation for coupling with intermittent electrical sources. The membrane separator also enables the use of pure water rather than supporting electrolyte, improving system safety, simplifying system- and plant-level engineering, and eliminating efficiency losses from shunt currents.<sup>7</sup> However, the locally acidic environment of the PEM necessitates more expensive catalysts (Ir, Pt, etc.) and hardware (Ti, etc.).

Anion-exchange-membrane (AEM) electrolysis is an emerging technology that, with further development, can combine the benefits of PEM and liquid-alkaline systems. AEM electrolyzers use an anion-selective hydroxide-conducting polymer membrane, which creates a locally alkaline environment that enables the use of non-PGM catalysts (Ni, Co, Fe, etc.) and flow fields (steel) while maintaining the ability to operate in pure water with low gas crossover (Fig. 1).<sup>8</sup> However, currently AEM technology is immature, and does not meet the performance and stability needed to compete with PEM. This limitation is largely due to the lack of a high-performing, stable anion-exchange polymer. Further, while many high-performing,

stable non-PGM catalysts for the oxygen-evolution reaction (OER) have been identified in lab-scale testing in KOH, this behavior hasn't directly translated to industrially relevant device operation in pure water.<sup>9,10</sup>

## Degradation of Anion Exchange Polymers

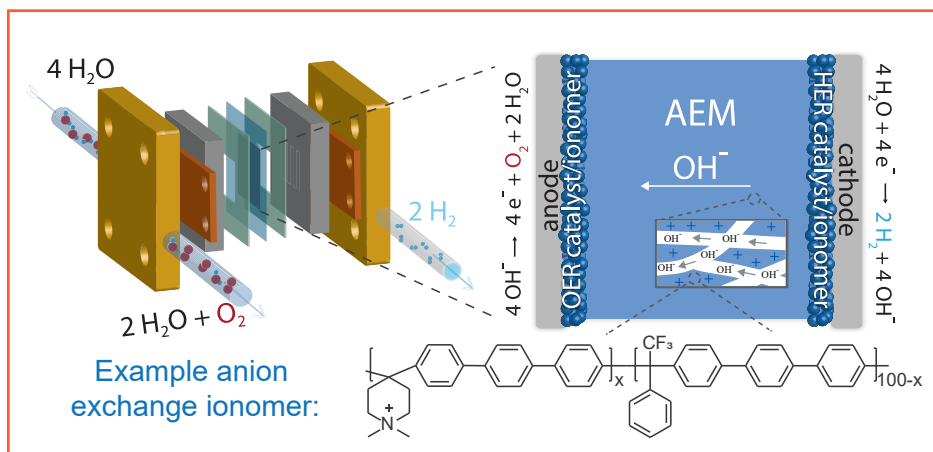
For AEM electrolyzers and fuel cells, the stability-limiting component is the anion exchange polymer.<sup>5</sup> This polymer is used as a membrane and mixed in the catalyst layer to transport hydroxide to the high-surface-area catalyst and improve contact between the catalyst layer and the membrane. Most polymer development has focused on improving polymer alkaline stability and prevention of OH<sup>-</sup> nucleophilic attack.<sup>11, 12</sup> The oxygen electrode in fuel cells, however, operates at much less-oxidizing potential than in electrolyzers, meaning the ionomers in electrolyzers must have much better oxidative stability. Polymer degradation experiments also often use model ex-situ studies, such as soaking materials in KOH solution or three-electrode studies mimicking oxidative environments.<sup>12, 13</sup>

When operating in an AEM electrolyzer with pure-water feed, the ionomer in the anode catalyst layer sees substantial oxidative damage. When testing different anion exchange polymers, a similar degradation rate occurs for the initial ~20 h of operation, nearly independent of polymer chemistry across a wide range of materials.<sup>14</sup> X-ray photoelectron spectroscopy (XPS) shows an increase in oxidized carbon content and a loss of cation groups (Fig. 2).<sup>14</sup> Kim and coworkers isolated phenyl oxidation to phenol in model studies,<sup>15</sup> and supporting computational work from Hendon and coworkers suggests the aromatic regions of the polymer are weak sites for oxidation.<sup>16</sup> The exact degradation mechanism is complicated, but likely includes both electrochemical reactivity by direct oxidation, perhaps coupled with OH<sup>-</sup> attack, of the polymer and chemical reactivity with oxygen radical species and other reactive OER intermediates.

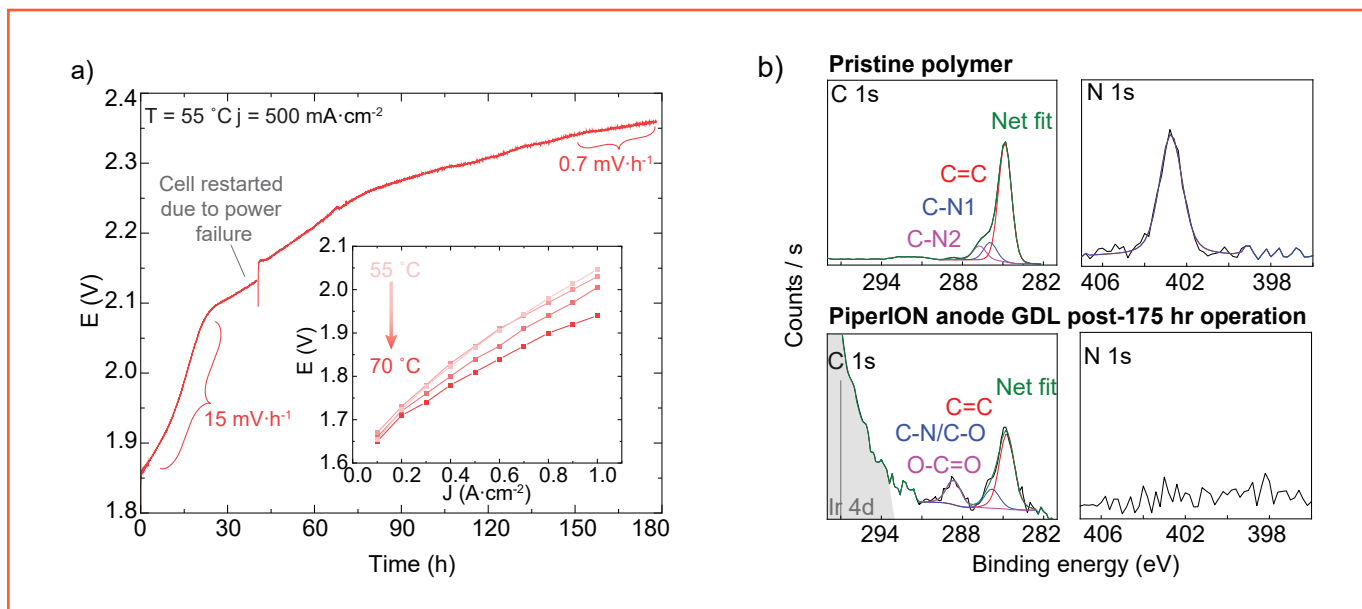
## Earth-abundant Oxygen-evolving Anode Catalysts

The activity of earth-abundant (particularly Ni, Fe, and Co-based) catalysts for OER has been extensively studied in alkaline conditions.<sup>17-19</sup> For all mixed-metal oxyhydroxides, and the oxides/sulfides/phosphides etc. that serve as pre-catalysts to the oxyhydroxides,<sup>20-22</sup> Fe is essential for high activity.<sup>23, 24</sup> Fe-containing Ni oxyhydroxides are the most active catalysts in alkaline media,<sup>25</sup> with turnover frequencies ten-fold higher than IrO<sub>x</sub>.<sup>26</sup> Co oxides/oxyhydroxides have a lower activity but are more structurally stable under OER conditions. The active catalyst's phases in both cases are typically molecular-scale metal oxo-/hydroxo species that under OER conditions oxidize from a nominally layered double hydroxide to an oxyhydroxide structure. The transition metal oxidation (i.e., Ni<sup>2+</sup> to Ni<sup>3+</sup>), is generally accompanied by a large increase in electrical conductivity, which contributes to the high performance.<sup>19</sup>

While structure-composition-performance relationships have been



**FIG. 1. AEMWE schematic.** An anion-selective hydroxide conducting membrane is sandwiched between two gas diffusion electrodes (GDEs) coated with a HER or OER catalyst and anion exchange ionomer. Adapted from ref. 8.



**Fig. 2. Electrolyzer degradation.** a) Pure-water fed AEM electrolyzer durability. The inset shows temperature-dependent initial performance. b) XPS comparison of polymer in a pristine and operated anode. Adapted from ref. 14.

identified in three-electrode studies with a supporting electrolyte, it is unclear how these translate to AEM devices fed with pure water. Despite their high OER activity, Ni-Fe-based catalysts tend to show poor activity and stability in a pure-water membrane-electrode assembly (MEA) environment.<sup>10</sup> We found that NiFe<sub>2</sub>O<sub>4</sub> nanoparticles failed rapidly during electrolyzer testing, but Co<sub>3</sub>O<sub>4</sub> nanopowders performed the best out of all non-PGM catalysts tested and showed comparable performance and stability to high-surface area commercial IrO<sub>3</sub> (Fig 3).<sup>9</sup> XPS analysis showed that the least-stable catalysts undergo significant surface transformation during operation (Fig. 3d). The electrolyzer operating voltages trended with the dry powder electrical conductivity (Fig. 3c), indicating that the catalysts were limited by electronic conductivity and not fully restructuring to the conductive oxyhydroxide phase during operation. This observation is likely due to the use of an anion exchange ionomer to supply OH<sup>-</sup> ions rather than a supporting electrolyte. The hydroxide is confined to near the ionomer cationic backbone and it is not able to transport through the layered sheets, inhibiting the chemical transformation.

We attribute the better performance of Co<sub>3</sub>O<sub>4</sub> to its high electrical conductivity and resistance to structural rearrangement during operation. Notably, others have shown Ni-Fe oxide catalysts perform well in AEM devices when fed with KOH<sup>27, 28</sup> or in pure water when using a thin layer of NiFe catalyst on a conductive supporting substrate that compensates for the poor electronic conductivity of the material when not fully converted to the oxyhydroxide form.<sup>29, 30</sup>

## Perspective and Outlook

AEM electrolysis is positioned to play a key role in the predicted exponential growth of green hydrogen technology with essential R&D advances in the coming years. We revealed key design parameters essential to commercialization. First, stable alkaline OER catalysts with high electronic conductivity and minimal surface reconstruction during operation must be designed. Alkaline catalyst layers must also be applied to the MEA with scalable, industrially relevant techniques. Second, ionomer oxidation mitigation strategies must be developed. This approach could also target other creative catalyst layer design, such as phase-separation control to protect oxidation-prone organic components or catalyst engineering to direct selectivity for hydroxide over polymer oxidation. If competitive efficiency and durability can be achieved in pure water, AEM electrolysis has the potential to become a dominant electrolyzer technology.

## Acknowledgements

The authors acknowledge support from the US Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Fuel Cell Technologies Office (FCTO) award DE-EE0008841 and the John Keana Research Fellowship from the University of Oregon.

© The Electrochemical Society. DOI: 10.1149/2.F05232IF

## About the Authors



**GRACE LINDQUIST, OREGON CENTER FOR ELECTROCHEMISTRY, DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY, UNIVERSITY OF OREGON**

**Education:** BA in Chemistry (College of Saint Benedict and Saint John's University), PhD in Chemistry under Prof. Shannon Boettcher at the University of Oregon.

**Research Interests:** Water electrolysis, Catalysis, Ion exchange polymer materials

**Pubs + Patents:** 11 first- and co-author papers, 9 conference and workshop presentations, 1 provisional patent, h-index 6.

**Awards:** ECS Energy Technology Division Graduate Student Award (2021), Keana Fellow (2020), Dean's First Year Merit Scholar (2018)

**Work with ECS:** Energy Technology Division student member since 2020

**Website:** <https://boettcher.uoregon.edu/current-members-boettcher-lab/members-v3/>

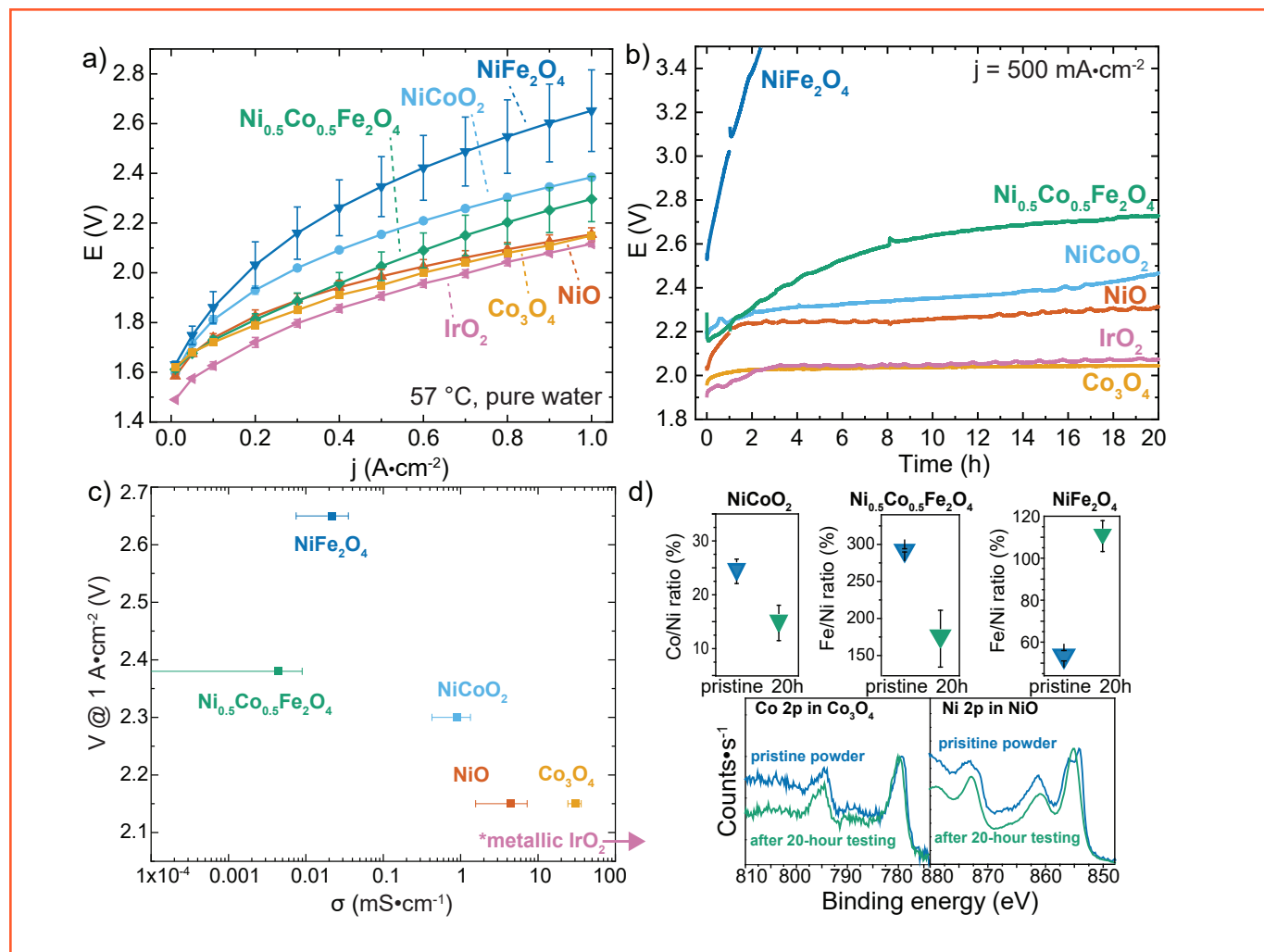
**ORCID:** <https://orcid.org/0000-0001-5896-2331>



**SHANNON BOETTCHER, PROFESSOR, OREGON CENTER FOR ELECTROCHEMISTRY, DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY, UNIVERSITY OF OREGON**

**Education:** BA Chemistry (physics emphasis) at the University of Oregon, PhD in Inorganic Materials Chemistry under Galen Stucky, NSF Graduate Research Fellow and Chancellor's Fellow, UC Santa Barbara.

(continued on next page)



**FIG. 3. Non-PGM catalyst operation.** a) Polarization curves of anode catalysts tested. All experiments were conducted in pure water at  $57^\circ\text{C}$ . A stainless-steel woven substrate with the indicated catalyst was used as the anode GDL and Pt black catalyst on Toray carbon paper was used as the cathode GDL. b) Durability testing for each catalyst held at  $500 \text{ mA}\cdot\text{cm}^{-2}$ . c) Electrical conductivity of dry powders measured in a pressed pellet. d) The change in metal ratios of mixed-metal catalysts and changes to Co 2p in  $\text{Co}_3\text{O}_4$  and Ni 2p in  $\text{NiO}$  determined by XPS. All catalysts were operated for 20 h at  $500 \text{ mA}\cdot\text{cm}^{-2}$ . Adapted from ref. 9.

**Work Experience:** Professor in the Department of Chemistry and Biochemistry at the University of Oregon. His research is at the intersection of materials science and electrochemistry, with a focus on fundamental aspects of energy conversion and storage. In 2019 he founded the Oregon Center for Electrochemistry and the first graduate program in Electrochemical Technology in the USA.

**Research Interests:** Electrochemistry, Solar energy, Solid state materials chemistry, Catalysis

**Pubs + Patents:** 143 publications, >150 invited talks and lectures, 8 patents, h-index 62 and ISI Highly Cited Researcher (top ~0.1%) (2019, 2020, 2021, 2022).

**Awards:** Blavatnik National Award Finalist (top 10 in chemistry, 2021), Camille Dreyfus Teacher Scholar Award (2015), Sloan Fellowship (2015)

**Work with ECS:** ECS Member for ~10 years; founding member of PNW ECS Chapter (treasurer)

**Website:** <https://boettcher.uoregon.edu/>

**ORCID:** <https://orcid.org/0000-0001-8971-9123>

## References

1. Hydrogen Council, Path to hydrogen competitiveness: A cost perspective (2020). Accessed Dec. 2022 <https://hydrogencouncil.com/en/path-to-hydrogen-competitiveness-a-cost-perspective/>
2. IEA, The future of hydrogen; IEA: Paris (2019).
3. A. Kusoglu, *Electrochem. Soc. Interface*, **30**, 44 (2021).
4. P. A. Kempler, J. J. Slack, and A. M. Baker, *Joule*, **6**, 280 (2022).
5. K. Ayers, N. Danilovic, R. Ouimet, M. Carmo, B. Pivovar and M. Bornstein, *Annu. Rev. Chem. Biomol. Eng.*, **10**, 219 (2019).
6. M. R. Kraglund, M. Carmo, G. Schiller, S. A. Ansar, D. Aili, E. Christensen and J. O. Jensen, *Energy & Environmental Science*, **12**, 3313 (2019).
7. M. Carmo, D. L. Fritz, J. Mergel and D. Stolten, *Int. J. Hydrogen Energy*, **38**, 4901 (2013).
8. G. A. Lindquist, Q. Xu, S. Z. Oener and S. W. Boettcher, *Joule*, **4**, 2549 (2020).
9. R. A. Krivina, G. A. Lindquist, S. R. Beaudoin, et al., *Adv. Mater.*, **34**, 2203033 (2022).
10. D. Xu, M. B. Stevens, M. R. Cosby, et al., *ACS Catal.*, **9**, 7 (2019).
11. C. G. Arges and L. Zhang, *ACS Appl. Energy Mater.*, **1**, 2991 (2018).

12. K. F. L. Hagesteijn, S. Jiang, and B. P. Ladewig, *J. Mater. Sci.*, **53**, 11131 (2018).
13. H. Cao, J. Pan, H. Zhu, Z. Sun, B. Wang, J. Zhao, and F. Yan, *Adv. Sci.*, **8**, 2101744 (2021).
14. G. A. Lindquist, S. Z. Oener, R. Krivina, et al., *ACS Appl. Mater. Interfaces*, **13**, 51917 (2021).
15. D. G. Li, I. Matanovic, A. S. Lee, E. J. Park, C. Fujimoto, H. T. Chung, and Y. S. Kim, *ACS Appl. Mater. Interfaces*, **11**, 9696 (2019).
16. R. A. Krivina, G. A. Lindquist, M. C. Yang, et al., *ACS Appl. Mater. Interfaces*, **14**, 18261 (2022).
17. C. C. L. McCrory, S. Jung, J. C. Peters, and T. F. Jaramillo, *J. Am. Chem. Soc.*, **135**, 16977 (2013).
18. B. M. Hunter, H. B. Gray, and A. M. Müller, *Chem. Rev.*, **116**, 14120 (2016).
19. M. B. Stevens, L. J. Enman, E. H. Korkus, et al., *Nano Res.*, **12**, 2288 (2019).
20. E. Fabbri, M. Nachtegaal, T. Binninger, et al., *Nat. Mater.*, **16**, 925 (2017).
21. K. Wang, X. Wang, Z. Li, et al., *Nano Energy*, **77**, 105162 (2020).
22. J. Mohammed-Ibrahim, *J. Power Sources*, **448**, 227375 (2020).
23. L. Trotochaud, S. L. Young, J. K. Ranney, and S. W. Boettcher, *J. Am. Chem. Soc.*, **136**, 6744 (2014).
24. M. B. Stevens, C. D. M. Trang, L. J. Enman, J. Deng, and S. W. Boettcher, *J. Am. Chem. Soc.*, **139**, 11361 (2017).
25. M. S. Burke, S. Zou, L. J. Enman, J. E. Kellon, C. A. Gabor, E. Pledger, and S. W. Boettcher, *The J. Phys. Chem. Lett.*, **6**, 3737 (2015).
26. L. Trotochaud, J. K. Ranney, K. N. Williams, and S. W. Boettcher, *J. Am. Chem. Soc.*, **134**, 17253 (2012).
27. I. Vincent, E.-C. Lee, and H.-M. Kim, *Sci. Rep.*, **11**, 293 (2021).
28. N. Chen, S. Y. Paek, J. Y. Lee, J. H. Park, S. Y. Lee, and Y. M. Lee, *Energy Environ. Sci.*, **14**, 6338 (2021).
29. J. Xiao, A. M. Oliveira, L. Wang, et al., *ACS Catal.*, **11**, 264 (2021).
30. F. Razmjooei, T. Morawietz, E. Taghizadeh, et al., *Joule*, **5**, 1776 (2021).

## About the Editor



**SCOTT CUSHING, ASSISTANT PROFESSOR OF CHEMISTRY, CALTECH**

**Education:** BS in Physics, emphasis in Material Science and Chemistry and PhD in Physics, under Nick Wu and Alan Bristow (West Virginia University).

**Research Interests:** With a multidisciplinary background spanning Chemistry, Materials Science, and Physics, his research focuses on the creation of new scientific instrumentation

that can translate quantum phenomena to practical devices and applications. The Cushing lab is currently pioneering the use of attosecond x-ray, time-resolved TEM-EELS, and ultrafast beams of entangled photons for a range of microscopy and spectroscopy applications.

**Work Experience:** Past appointments include Dept. of Energy EERE Postdoctoral Fellow, Prof. Stephen Leone Group University of California, Berkeley with a Co-Appointment at Lawrence Berkeley National Laboratory. Currently Senior Research Advisor for Pacific Integrated (PI) Energy, San Diego, CA.

**Pubs & Patents:** >60 publications, 3 patents, h-index >30, cited ~8,000 times

**Awards:** 2022 Cottrell Scholar, 2022 Shirley Malcom Prize for Excellence in Mentoring, 2019–2021 Young Investigator awards for DOE, AFOSR, ACS, and Rose Hill Foundation.

**Work with ECS:** ETD Division: assist with organizing and chairing symposium. Member for >15 years.

**Website:** [cushinglab.caltech.edu](http://cushinglab.caltech.edu)

 <https://orcid.org/0000-0003-3538-2259>

# MEDIA GUIDE

Integrated  
Advertising Solutions

*See online NOW!*

Contact [Sponsorship@electrochem.org](mailto:Sponsorship@electrochem.org) today!

 The Electrochemical Society  
Advancing solid state & electrochemical science & technology



# 2023 ECS INSTITUTIONAL MEMBERS

## BENEFACTOR

BioLogic USA/BioLogic SAS (15\*)  
Duracell US Operations, Inc. (66)  
Gamry Instruments (16)  
Gelest Inc. (14)  
Hydro-Québec (16)  
Pine Research Instrumentation (17)

## PATRON

Energizer Battery (78)  
Faraday Technology, Inc. (17)  
GE Global Research Center (67)  
Lawrence Berkeley National Laboratory (LBNL) (19)  
Scribner Associates (27)  
Toyota Research Institute of North America (TRINA) (15)

## SPONSORING

BASi (8)  
Center for Solar Energy and Hydrogen Research Baden-Württemberg (ZSW) (19)  
Center for Synthetic Organic Electrochemistry, University of Utah (2)  
Central Electrochemical Research Institute (30)  
Corteva Agriscience (1)  
Deutsches Zentrum für Luft- und Raumfahrt e.V. (DLR) (15)  
Electrosynthesis Company, Inc. (27)  
EL-CELL GmbH (9)  
Ford Motor Company (9)  
GS Yuasa International Ltd. (43)  
Honda R&D Co. (16)  
Medtronic, Inc. (43)  
Nissan Motor Co., Ltd. (16)  
Pacific Northwest National Laboratory (PNNL) (4)  
Panasonic Energy Corporation (28)  
Permascand AB (20)  
Plug Power, Inc. (2)  
Teledyne Energy Systems, Inc. (24)  
UL Research Institutes (2)

## SUSTAINING

Advanced Cell Engineering (2)  
Cummins, Inc. (5)  
Current Chemicals (1)  
General Motors Holdings LLC (71)  
Giner, Inc. (37)  
Ion Power, Inc. (9)  
Kanto Chemical Co., Inc. (11)  
Los Alamos National Laboratory (LANL) (15)  
Metrohm USA, Inc. (9)  
Microsoft Corporation (6)  
Occidental Chemical Corporation (81)  
Sandia National Labs (47)  
Sherwin-Williams (2)  
Spectro Inlets ApS (1)  
Technic, Inc. (27)  
United Mineral & Chemical Corporation (2)  
Western Digital GK (9)  
Westlake Corporation (28)  
Yeager Center for Electrochemical Sciences at CWRU (25)

Please help us continue the vital work of ECS by joining as an institutional member today.  
To renew, join, or discuss institutional membership options please contact  
**Anna Olsen, Senior Manager, ECS Corporate Programs, [anna.olsen@electrochem.org](mailto:anna.olsen@electrochem.org).**