Energy Spotlight

New Insights into Perovskites, CO₂ Electrolysis, and 3D Porous Electrodes

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Our editorial advisory board members Aron Walsh, Shannon W. Boettcher, Jun Lu, and Brian Seger present highlights of three articles published in the October issue. They highlight new insights into phase segregation in mixed-halide perovskites, the importance of understanding local pH in analyzing and optimizing CO₂ electrolysis, and interfacial activity gradient (IAG) to enable the bottom-up Li growth in three-dimensional (3D) porous frameworks for next-generation rechargeable batteries.

■ LATTICE COMPRESSION INCREASES THE ACTIVATION BARRIER FOR PHASE SEGREGATION IN MIXED-HALIDE PEROVSKITES (LETTER)

Loreta A. Muscarella, Eline M. Hutter, Francesca Wittmann, Young Won Woo, Young-Kwang Jung, Lucie McGovern, Jan Versluis, Aron Walsh, Huib J. Bakker, and Bruno Ehrler
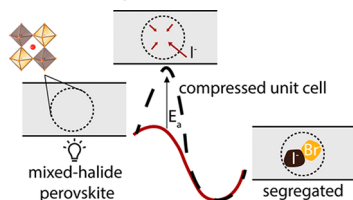
The longer we look at metal halide perovskites, the more complicated they become. They do adopt the perovskite structure type, but perhaps only when averaged over space or time. If you take a snapshot, the individual bond lengths and angles are likely to deviate far from their ideal values. Some ions will be caught far from their regular lattice sites. There are growing reports of chemical and structural inhomogeneities across multiple length scales even in high-quality thin films [*Nature* 2020, 580, 360]. There is also evidence that the crystal structures are modified in response to mild external perturbations, including light and electric fields.

The role of pressure has been explored in several metal halide perovskites. Pressure can modify the crystal structure, as well as the magnitude and type of the band gap [*Energy Environ. Sci.* 2017, 10, 509]. However, can it also be used as a lever to control the stability and lifetimes of mixed perovskites? Bruno Ehrler and collaborators probe the impact on CH₃NH₃Pb(I,Br)₃ using pressure-dependent transient absorption spectroscopy as a probe for phase separation. Remarkably, they find that a pressure of just 0.3 GPa can strongly suppress the kinetics of I,Br domain growth under illumination. This behavior is linked to the relatively high compressibility of the metal halide crystals. My group had a small role, confirming from first-principles simulations that pressure increases the activity energy for vacancy-assisted halide diffusion. An important conclusion from this study is that cation engineering can be used to realize the same effect. Similar to the application of external pressure, Cs substitution can reduce the lattice spacing and hence suppress ion mobility. This opens up an intriguing avenue for increasing the window of accessibility for mixed-halide perovskites.
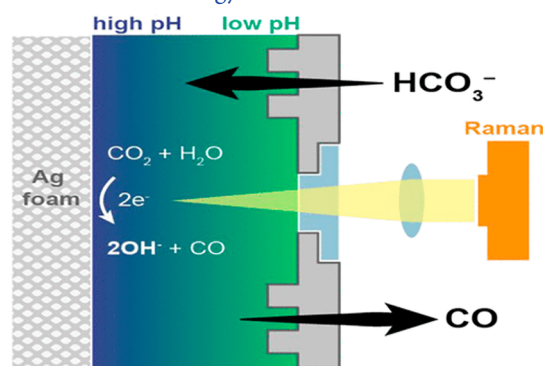
Aron Walsh

■ pH MATTERS WHEN REDUCING CO₂ IN AN ELECTROCHEMICAL FLOW CELL (LETTER)

Zishuai Zhang, Luke Melo, Ryan P. Jansonius, Faezeh Habibzadeh, Edward R. Grant, and Curtis P. Berlinguette
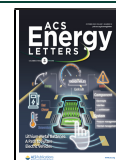
CO₂ electrolysis has the potential to mimic water electrolysis, except it has the benefit that it uses the major greenhouse gas as a reactant and can produce a multitude of products with higher value than hydrogen. While the potential to produce CO₂-derived chemicals and fuels is immense, so are the challenges when working with CO₂ electrolysis. A major

complexity in CO_2 electrolysis is the fact that CO_2 dissolves in water, forming either bicarbonate or carbonate dependent upon pH. This equilibrium, along with the fact that the reaction stoichiometry of CO_2 electrolysis entails hydroxides will be produced, greatly complicates the pH situation throughout the device. With activity, selectivity and mass-transfer issues all significantly affected by pH, understanding local pH is essential for analyzing and optimizing CO_2 electrolysis.

The work by Zhang et. al (*ACS Energy Lett.* **2020**, *5*, 3101−3107) provides a clever way to monitor the local pH by using Raman spectroscopy to measure carbonate and bicarbonate concentrations during testing. Because the equilibrium between these two species is dependent on pH, comparing their peak intensities allows an in situ technique to determine the local pH within the device. By controlling the focal height of the Raman signal, the authors were able to show this technique can provide a profile of the pH as a function of depth from the catalyst. With a multitude of different engineering designs and approaches being investigated to maximize performance, this technique provides a highly useful tool for researchers to understand and optimize the pH profile within their device.

Brian Seger

Driving *any* electrochemical reaction that generates or consumes protons will result in a pH gradient from the electrode surface moving into the electrolyte. The magnitude of this pH gradient will depend on a number of factors, including the current density (which is proportional to the rate of H^+ generation or consumption), the concentration and diffusion coefficient of any species that can transport protons (e.g., H^+, OH^-, or buffers), and any convective mass transport phenomena (e.g., flow, stirring, or bubble-induced convection). In water electrolysis, strongly acidic or basic conditions are used, which lead to small pH gradients. In CO_2 electrolysis, however, acidic conditions lead to preferential H_2 production over CO_2 reduction at the cathode, dramatically lowering faradaic efficiency. Under strongly basic conditions, CO_2 is converted to CO_3^{2-}, consuming the base which must then be replenished. Therefore, CO_2 electrolysis is typically performed under buffered conditions with bicarbonate electrolyte; understanding the exact local pH at the electrode surface, and how to optimize it for catalytic and faradaic efficiency, is important.

Writing in this issue of *ACS Energy Letters*, Zhang et. al report a Raman-spectroscopy-based method to measure pH gradients in a CO_2 electrolyzer flow cell—a type of practical electrolyzer geometry—that has much different mass transport behavior than, for example, related H-cells. They discover pH gradients that depend on current density with the surface of a Ag foam electrode at pH ~10.5 at 200 mA cm^{-2} while the pH of the bulk solution at the outside of the diffusion layer (~0.2 mm) is substantially lower, ~8.5. This gradient occurs because the cathode reaction consumes protons and for the "bulk" solution to provide the needed inward flux of HCO_3^- requires a concentration gradient governed largely by Fick's first law $J_{diffusion} = -D_i \cdot dC_i/dx$, where, for species i, $J_{diffusion}$ is the flux, D_i the diffusion coefficient, and C_i the concentration. It would be interesting to further probe the local pH within the Ag foam electrode used, ~0.2 mm in thickness, and how that pH changes with distance from the bipolar membrane used to separate the anode and cathode. Other, nonoptical, methods are likely needed for such experiments.

When the temperature was increased, the concentration gradient also increased, despite the fact that the diffusion coefficient for HCO_3^- should increase and thus lower the gradient necessary to maintain the flux at steady state. Other effects, such as those associated with the CO_2 hydration/dehydration kinetics, could be at play. Over time, the authors see the bulk pH increase indicating a net consumption of protons. This could be due to the dehydration of bicarbonate, $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$, consuming protons with some of the CO_2 lost with the output reduction product, CO. The dehydration reaction rate would increase dramatically with temperature, perhaps explaining the higher local pH at the electrode observed at 70 °C as compared to 20 °C. Combined ion transport (and not selective H^+ or OH^-) through the bipolar membrane might also be important. In any case, this increase in local pH (beneficially) decreased the faradaic efficiency for hydrogen evolution.

From the authors data and analysis it is clear that complex effects are at play that determine the precise local pH and how it depends on electrolysis, electrolyte, and flow parameters. *Operando* techniques that report on local pH and allow for the development of accurate electrolyzer models, such as reported here, are thus quite important for this field.
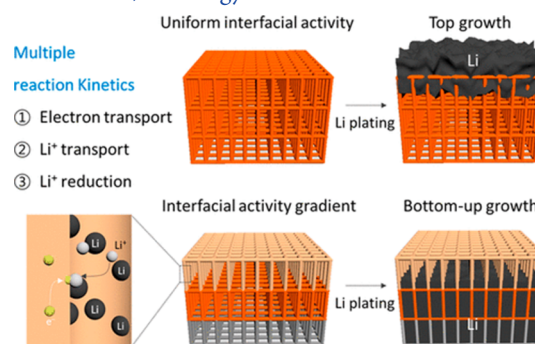
Shannon W. Boettcher

■ BOTTOM-UP LITHIUM GROWTH TRIGGERED BY INTERFACIAL ACTIVITY GRADIENT ON POROUS FRAMEWORK FOR LITHIUM−METAL ANODE (LETTER)

Jonghyeok Yun, Beom-Kyeong Park, Eun-Seo Won, Seung Hyun Choi, Hyon Chol Kang, Jung Ho Kim, Min-Sik Park, and Jong-Won Lee

The use of Li metal anode has been gradually recognized as one of the most efficient and feasible strategies for pursuit of high-energy rechargeable lithium ion batteries. To address the existing problems such as large volume variation and presence of peak local current densities upon cycling, a three-dimensional (3D) porous framework has been recently explored as an advanced host for Li$^+$. However, such design, because of the significantly increased dimension along the Li$^+$ flow direction, has been inevitably plagued by the uneven Li plating−stripping kinetics caused by the intrinsically sluggish Li$^+$ diffusion kinetics within the electrolyte filling the 3D pores. Consequently, this seemingly efficient strategy is severely compromised by the commonly seen preferable Li plating on top of the framework instead of deep into the electrode bottom.

A recent work led by Yun et al. reported the achievement of bottom-up plating of Li metal in 3D Cu-based porous framework by properly tuning the interfacial Li growth activity with respect to the depth of the electrode host. Inspired by their simulation result showing effective interfacial activity gradient (IAG) achieved via a combination of bottom activation and top passivation of the 3D host, the authors of this work further carried out experiments to test their hypothesis. The bottom activation of the host was achieved via deposition of lithiophilic Ag while the top passivation simply utilized dip-coating of insulative PVDF. Through the synergistic effect of both methods, the IAG design demonstrated well-regulated growth of Li in the 3D Cu host; that is, Li was successfully controlled to be first plated at the bottom of the host from where it continued to grow gradually to the top part, which thus makes the pore space of the 3D host fully utilized for reversible Li storage. With the demonstrated satisfying structural stability, high coulombic efficiency, and limited negative effect of SEI, the IAG method reported in this work is expected to provide a base for the design and modification of an advanced 3D host for Li storage.

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Notes
The authors declare no competing financial interest.
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