

Energy Spotlight

Advances in Tin Halide Perovskite Solar Cells, Electrocatalytic CO₂ Reduction and Lithium–Air Batteries



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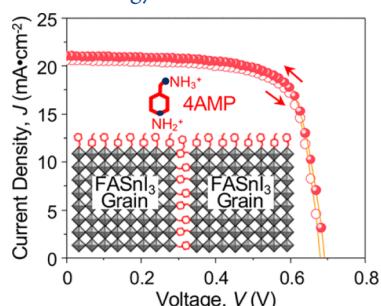
Our editorial advisory board members Marina Leite, Csaba Janáky, and Nam-Soon Choi present highlights of June–July articles. They spotlight new advances in energy research that include development of lead-free perovskite solar cells, implementation of the BPM membrane for CO₂-to-formate conversion, and optimization of electrolytes for lithium–oxygen and lithium–air batteries.

■ HIGH-PERFORMANCE LEAD-FREE SOLAR CELLS BASED ON TIN-HALIDE PEROVSKITE THIN FILMS FUNCTIONALIZED BY A DIVALENT ORGANIC CATION (LETTER)

Min Chen, Qingshun Dong, Felix T. Eickemeyer, Yuhang Liu, Zhenghong Dai, Alexander D. Carl, Behzad Bahrami, Ashraful H. Chowdhury, Ronald L. Grimm, Yantao Shi, Qiquan Qiao, Shaik Mohammed Zakeeruddin, Michael Grätzel, Nitin P. Padture

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The search for high-performing, stable, and nontoxic perovskite solar cells has been a “holy grail” objective in photovoltaics for the past decade. A current major challenge in the field is to replace Pb by an alternative, such as Sn, Bi, Ge, or Ti. From all options investigated to date, Sn-based devices have shown the most promising results. Yet, halide perovskites containing Sn are usually unstable when exposed to humidity and oxygen and are notoriously known for being highly defective. Therefore, there is a pressing need for demonstrating Sn-based solar cells that can uphold good performance. Padture (Brown University) and co-workers present a significant step toward the development of Sn-based photovoltaics in this issue of *ACS Energy Letters*. By adding a divalent organic cation, 4-(aminomethyl)-piperidinium (4AMP), onto formamidinium tin triiodide (FASnI₃) perovskites they show devices with power conversion efficiency >10%

and >70% retention of performance over 500 h under continuous illumination. The 4AMP molecules fully functionalize the perovskite grains, including its boundaries, suppressing the diffusion of H₂O and O₂ onto its lattice. A value of 15 mol % 4AMP was found to be a good balance between enough molecules to promote effective functionalization and a small enough amount to suppress the formation of the deleterious low-dimensional Dion–Jacobson phase. This hypothesis was confirmed by measuring spectral photon flux and photoluminescence lifetime while comparing the effect of 4AMP concentration on the perovskites’ optical response. Moreover, X-ray diffraction showed that the functionalized Sn-based thin-film perovskites are preserved upon exposure to ambient air with ~50% relative humidity for 12 h. This work provides an inspiring route for engineering the surface of Pb-free halide perovskites to enable devices with superior performance. Material chemistry will likely continue to play an important role in the pursuit of environmentally friendly perovskite solar cells.

Marina Leite

■ A ROBUST, SCALABLE PLATFORM FOR THE ELECTROCHEMICAL CONVERSION OF CO₂ TO FORMATE: IDENTIFYING PATHWAYS TO HIGHER ENERGY EFFICIENCIES (LETTER)

Yingying Chen, Ashlee Vise, W. Ellis Klein, Firat C. Cetinbas, Deborah J. Myers, Wilson A. Smith, Todd G. Deutsch, K. C. Neyerlin

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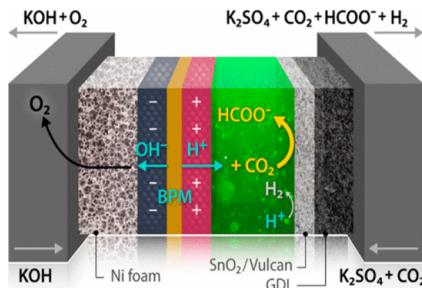


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Employing ion-exchange membranes to separate the two half-cells in CO_2 electrolysis has multiple benefits, compared to a microfluidic scenario, where only a liquid electrolyte separates the two electrodes. At the same time, to date, there is no optimal choice of membrane. Cation exchange membranes typically enhance the parasitic hydrogen evolution reaction, while in the case of anion exchange membranes the crossover of carbonate and bicarbonate ions limits the achievable conversion efficiency. Bipolar membranes (BPMs) in principle can mitigate both of the above issues for a given energy penalty (because of the increased resistance of the cell). Despite some pioneering studies, high current density operation with BPMs is rare, especially at a cell size where edge effects and other artifacts are less relevant.

In their new study, K. C. Neyerlin et al. demonstrate a viable approach for implementing the BPM membrane concept for CO_2 -to-formate conversion. One major novelty of the presented cell architecture is the tunable catholyte layer thickness between the cation exchange layer of the BPM and the cathode. This optimization is crucial to successfully balance among the necessary buffering effect, maximizing CO_2R selectivity and minimizing resistive ohmic losses. With a relatively large catholyte thickness (1.27 mm), this cell converted CO_2 to formate at a rate of 500 mA/cm^2 at a gas diffusion electrode (25 cm^2) with carbon supported SnO_2 electrocatalyst. The bipolar membrane also successfully prevented formate crossover. Nanotomography analysis of the gas-diffusion electrode before and after operation (11 h) indicated changes in the catalyst agglomerate size and aspect ratio, which indicates that further work is necessary to enhance stability and/or durability.

The cell voltage (and therefore the energy efficiency) is still high (over 5 V at high current density), but the voltage loss contributions from individual components of the electrochemical cell were subsequently deconvoluted. This is a significant result, because such information will help the community to identify pathways to improve the energy efficiency of the whole CO_2 conversion process, via catalyst design and membrane/electrode/reactor engineering. The first step will certainly be the substantial reduction of the catholyte layer thickness.

Csaba Janáky

■ OPTIMIZED ELECTROLYTE WITH HIGH ELECTROCHEMICAL STABILITY AND OXYGEN SOLUBILITY FOR LITHIUM–OXYGEN AND LITHIUM–AIR BATTERIES (LETTER)

Won-Jin Kwak, Sujong Chae, Ruozhu Feng, Peiyuan Gao, Jeffrey Read, Mark H. Engelhard, Lirong Zhong, Wu Xu, Ji-Guang Zhang

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Advantages of LHCE

- ▲ Highly stable to ${}^1\text{O}_2$
- ▲ Highly stable to Li metal
- ▲ High oxygen solubility
- ▲ Low viscosity
- ▲ Good wetting
- ▲ Low cost

Aprotic lithium–oxygen ($\text{Li}–\text{O}_2$) batteries that are based on the electrochemical formation and decomposition of lithium peroxide (Li_2O_2) can provide extremely high energy density. However, their stable operation is largely restricted because most organic electrolytes are highly susceptible to decomposition on Li-metal surfaces and parasitic reactions with reactive oxygen species (singlet oxygen) generated from decomposing Li_2O_2 . Adopting electrolyte additives in batteries has been widely regarded as an effective way to provide protective barriers that inhibit undesirable side reactions between the electrodes and the electrolytes. Nevertheless, because the oxygen/air electrode should provide channels for rapid oxygen and Li ion mass transport and because its abundant active sites must be exposed, the construction of a passivation layer on the oxygen/air electrode is not desirable. In addition, limited oxygen solubility in the electrolyte and the evaporation of electrolyte solvents raised by the oxygen/air flow during cycling largely hinder the reversible operation of the $\text{Li}–\text{O}_2$ batteries. Previously reported additives and localized high-concentration electrolytes (LHCEs) did not simultaneously satisfy the requirements of oxygen solubility and electrolyte stability.

Zhang et al. provided insights into designing highly stable electrolyte systems that did not need additives, for high-performance $\text{Li}–\text{O}_2$ batteries. They integrated a solvating solvent and a diluent solvent that had improved stabilities with both the Li metal anode and the oxygen/air electrode. In particular, a fluorinated compound with high affinity toward oxygen gas was successfully employed as an electrolyte solvent, which enabled the facile dissolution of oxygen from air atmospheres and enhanced the performance of $\text{Li}–\text{O}_2$ batteries. The authors confirmed that LHCEs with an inert fluorinated diluent solvent with low volatility and high oxygen solubility are highly suitable for $\text{Li}–\text{O}_2$ batteries, especially when considering the reaction energies of the parasitic reactions with singlet oxygen and the oxidation potentials at the oxygen/air electrode. The concept of LHCEs including the solvating solvent and the fluorinated diluent solvent offers a promising direction for long-cycling $\text{Li}–\text{O}_2$ batteries.

Nam-Soon Choi

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Notes

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