

Energy Spotlight

Advances in Fundamental Li Electrochemistry and Energy Applications for Metal Organic Frameworks



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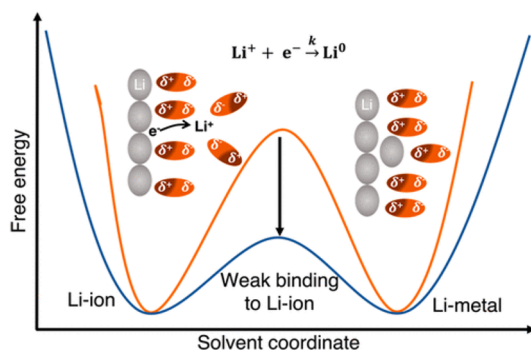
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Our EAB members, Drs. Shannon Boettcher, Jun Lu, and Nam-Soon Choi, highlight new advances in lithium-ion batteries and metal–organic frameworks for energy conversion and storage presented in two recently published papers in *ACS Energy Letters*.

■ TRANSIENT VOLTAMMETRY WITH ULTRAMICROELECTRODES REVEALS THE ELECTRON TRANSFER KINETICS OF LITHIUM METAL ANODES (LETTER)

David T. Boyle, Xian Kong, Allen Pei, Paul E. Rudnicki, Feifei Shi, William Huang, Zhenan Bao, Jian Qin, Yi Cui
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The use of metallic Li anodes provides a strategy to increase energy density in rechargeable Li-ion batteries. A key challenge is controlling both the solid–electrolyte–interphase (SEI) chemistry and preventing the formation of Li dendrites at high charge/discharge rates and over many cycles. Despite its apparent simplicity, the mechanism of the electrochemical reaction $\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$ is complicated and poorly understood. Historically, Butler–Volmer models have been used to provide a physical picture, but these models implicitly assume electron transfer through the electrochemical double layer. This is unlikely because it implies Li^0 forms in the electrolyte (e.g., at the outer Helmholtz plane). Boyle et al. combine ultramicroelectrode measurements with computational and analytical techniques to provide a new kinetic picture for Li deposition/stripping. They hypothesize that electron transfer to Li^+ at the inner Helmholtz plane (i.e., adsorbed on the surface) is rate-limiting. The potential dependence of the electron transfer rate is fit well by Marcus–Hush theory. The

reorganization energy varies with the solvent identity because of the different solvation energies of the Li^+ and with the identity of the counterion because of ion-pairing effects. Boyle's study therefore both advances the fundamental understanding of electrodeposition reactions in nonaqueous solvents as well as informs applied research in Li-metal anode development for high-energy-density batteries.

Shannon W. Boettcher EAB, *ACS Energy Letters*

High-energy-density lithium-ion batteries are urgently required, especially for the fast development of electric vehicles. The energy density would be greatly enhanced if the widely used graphite anode were replaced by metallic lithium. However, the wide application of lithium anodes has been severely limited because of its convoluted electrochemical processes, including the formation of the SEI, mass transport through the SEI, nucleation of lithium on current collectors, and interfacial electron transfer. Although there are numerous studies focused on SEI and dendrite formation of Li metal, little attention has been paid to how the electron-transfer kinetics would influence the lithium electrodeposition, which is critical to enable the practical application of lithium anodes. However, revealing the electron transfer kinetics has been challenging, as the measurements are heavily interfered with by the Li-ion transport through the SEI.

This technical challenge might now be conquered. A study led by Yi Cui et al. has demonstrated how to explicitly measure the electron transfer kinetics of $\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$ via transient cyclic voltammetry (CV) using ultramicroelectrodes. As the time scale of the transient CV measurement (<1 s) is much shorter than the time scale of passivation by an SEI, the influence of an SEI on the measurement can be minimized and the experiment can be carried out under electron transfer control at the lithium–electrolyte interface. In such a case, mass transport through the electrolyte or an SEI no longer controls the measurement. The authors found out that, in their newly designed electrode, electron transfer can be accurately

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described by Marcus models, rather than the commonly assumed Butler–Volmer model. Meanwhile, by exploring the electron-transfer kinetics in a series of electrolytes, they also found that the interaction between the solvent/anions with the Li ion and the viscosity of the electrolyte controls the rate of electron transfer. Moreover, by comparing the transient CV data to electrochemical impedance spectra (EIS) data, they were able to conclude that the electron-transfer resistance contributes to 0.12%–26% of the total interfacial resistance of lithium anodes.

Transient CV with ultramicroelectrodes provides a powerful tool to study the electron-transfer kinetics of lithium electrodeposition, which helps to interpret how the electron transfer and mass transfer would influence the morphology of electrodeposited lithium. The illumination of the mechanism of lithium electrodeposition should speed up the development of lithium batteries, especially the functional electrolytes.

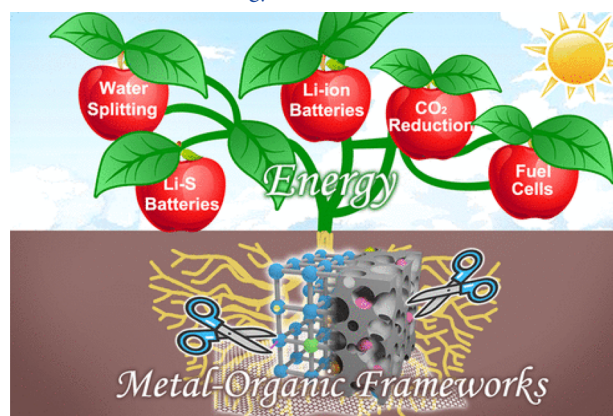
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METAL–ORGANIC FRAMEWORK-BASED MATERIALS FOR ENERGY CONVERSION AND STORAGE (REVIEW)

Tianjie Qiu, Zibin Liang, Wenhan Guo, Hassina Tabassum, Song Gao, and Ruqiang Zou

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Energy conversion and storage (ECS) technologies require significant advances in catalyst and electrode materials with proper electro- and photochemical characteristics. Metal–organic frameworks (MOFs) have compositional and structural benefits because of their highly ordered and tunable metal nodes and organic linkers that affect the efficiency and durability of ECS technology. In this regard, MOFs utilizing metal-containing nodes with organic bridges are regarded as up-and-coming components to modify catalysts, electrodes, and ionic conductors (electrolytes) for ECS.

In this Review, the authors discuss the potential and critical challenges of MOF-based materials for ECS. To confront the trade-offs that MOF-based materials face, rational component design and advanced nanostructuring focusing on 0D, 1D, 2D, and 3D structures are presented. Optimized component design (heterometallic doping, metal sites, and organic ligands) and a combination of functional components with MOFs can effectively overcome several limitations of individual components. For instance, although porous architectures are desirable to accommodate volume changes of electrode materials and facilitate electrolyte penetration into electrodes, the high

porosity of MOF-based materials leads to a low volumetric energy density for Li-ion batteries, which is detrimental to their practical use. An in-depth understanding of the roles of MOF-based materials offers effective strategies for enhanced stability for a wide range of application opportunities and helps overcome unexpected issues raised by interactions with other components introduced in ECS.

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Notes

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The authors declare no competing financial interest.