

Energy Spotlight

Advances in Lithium Batteries and Perovskite Solar Cells

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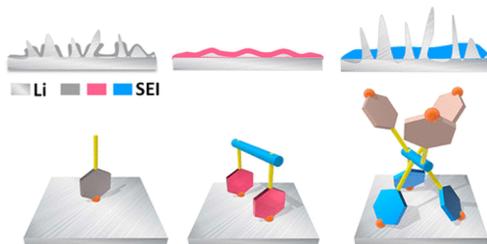
Three papers published in this issue of *ACS Energy Letters* are featured herein. These Letters discuss pyridine derivatives as electrolyte additives in Li-ion batteries (highlighted by Xiaolin Li), a helicene-based molecular hole-conducting material for perovskite solar cells (highlighted by Lioz Etgar), and charge-carrier mobility and localization in semiconducting $\text{Cu}_2\text{AgBiI}_6$ (highlighted by Omar Mohammed). These and other papers included in this issue provide exciting advances in energy research.

■ STABLE SOLID ELECTROLYTE INTERPHASE FORMATION INDUCED BY MONOQUAT-BASED ANCHORING IN LITHIUM METAL BATTERIES

Tianhong Zhou, Yan Zhao, Mario El Kazzi, Jang Wook Choi*, and Ali Coskun*

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Lithium is a unique metal with low atomic number, low density, high electromobility, and high reactivity. Batteries with Li metal anodes have the potential to deliver >500 Wh/kg specific energy and are considered the “holy grail” by many battery scientists. However, some of the unique features of Li metal, such as its high chemical and electrochemical reactivity, also have been the major obstacles to achieving a stably passivated Li–electrolyte interphase and hence have hampered the viability of commercial Li metal batteries because of safety and performance concerns.

In the work described in the *ACS Energy Letters* paper written by J. W. Choi and A. Coskun et al., molecules of pyridine derivatives, which are known to undergo simultaneous reduction reactions with alkali metals, have been utilized as electrolyte additives to create a homogeneous passivation layer on the surface of Li metal. The correlation between Li metal protection and subsequent electrochemical performance and the key structural parameters of the molecules, including the number and spatial arrangement of pyridine as well as the

number of positive charges, have been investigated. The pyridine derivative with the optimized molecular structure has an appropriate HOMO/LUMO energy and hence can have well-controlled reactivity with Li metal. With further optimization of the concentration in the electrolyte, it also can enable a high concentration of anions at the Li metal surface, which together with the anchor molecules facilitate the formation and homogeneous distribution of LiF throughout the reaction and the fast reaction kinetics with Li.

The solid electrolyte interphase layer is believed to be dense and to have high Li ion conductivity, ensuring good cycling performance of Li metal in both ether- and carbonate-based electrolytes. The symmetric cells in carbonate electrolyte demonstrated dendrite-free cycling over 350 cycles with 1 mAh/cm² cutoff capacity and 0.5 mA/cm² current density. The symmetric cells in ether electrolyte could deliver 250 dendrite-free cycles with 4 mAh/cm² cutoff capacity and 2 mA/cm² current density. This is a novel design for Li metal surface protection, and it can be a general strategy to passivate other electrodes with high reactivities and inhomogeneous morphology changes.

Xiaolin Li

■ A HELICENE-BASED MOLECULAR SEMICONDUCTOR ENABLES 85 °C STABLE PEROVSKITE SOLAR CELLS

Jianan Wang, Yiming Wang, Xinrui Xie, Yutong Ren, Bing Zhang, Lifei He, Jing Zhang, Li-Dong Wang, and Peng Wang*

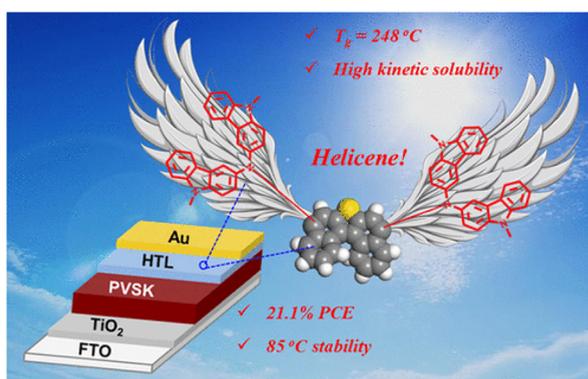
ACS Energy Lett. 2021, 6 (5), 1764–1772

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Perovskite solar cells can only be successful commercially when their durability and stability under an 85 °C thermal stress is improved. One of the key challenges in the structure of perovskite solar cells is related to the hole transport layer (HTL), which is responsible for instability issues in the solar cell. Intensive efforts have been directed to the development of HTLs for perovskite solar cells that will achieve high efficiency

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over 21% with excellent durability at 85 °C. To date, very few HTLs meet these requirements.

Two main factors are required from HTLs in order to provide high durability: (i) high glass temperature (T_g) and (ii) good solubility for solution process-ability.

In this work, Wang et al. have addressed these important issues by developing a HTL with high T_g , very good energy level alignment, excellent solubility, and efficient conductivity. They use quantum chemistry and molecular dynamics to simulate and synthesize a suitable HTL for thermostable perovskite solar cells. The new HTL is based on a helicene molecular semiconductor with improved T_g , high hole mobility, suitable HOMO level, and solubility in green solvents such as anisole. Moreover, the helicene molecular semiconductor demonstrates good resistivity to humidity.

The newly designed HTL shows a high efficiency of over 21%, retains its performance for 1000 h under aging conditions and for 500 h under continuous 1 sun illumination, and demonstrates 85 °C durability. This work not only opens the way to durable perovskite solar cells but also provides insight into the design of high-performance molecular semiconductors to be used as HTLs.

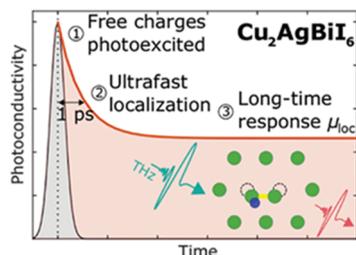
Lioz Etgar

■ CHARGE-CARRIER MOBILITY AND LOCALIZATION IN SEMICONDUCTING $\text{Cu}_2\text{AgBiI}_6$ FOR PHOTOVOLTAIC APPLICATIONS

Leonardo R. V. Buizza, Adam D. Wright, Giulia Longo, Harry C. Sansom, Chelsea Q. Xia, Matthew J. Rosseinsky, Michael B. Johnston, Henry J. Snaith, and Laura M. Herz*

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The recently discovered lead-free, wide-band-gap semiconductor $\text{Cu}_2\text{AgBiI}_6$ exhibits outstanding optical and transport properties, such as a high absorption coefficient, a high carrier mobility, a low-exciton binding energy, and long charge-carrier lifetime and diffusion length. These characteristics make it an excellent candidate not only to replace toxic lead perovskite structures but also to combine with silicon for tandem solar cells. Interestingly, the arrangement of atoms in

the structure of $\text{Cu}_2\text{AgBiI}_6$ is quite similar to that of standard ABX_3 perovskite chemical structures, and it exhibits both tetrahedral and octahedral geometries with the potential for chemical diversity, including additional compositional tuning to further enhance the optical and transport properties for light-harvesting applications. In other words, the uniqueness of the chemical structure of $\text{Cu}_2\text{AgBiI}_6$, with the cation-decorated cubic close-packed iodide array containing a Bi^{3+} ion, could provide diverse chemical approaches to control the optoelectronic properties beyond the family of lead perovskite structures.

The intrinsic optoelectronic properties of semiconductor absorber layers and their suitability for solar cell applications are determined by the nature of electron–phonon coupling and the localization of charge carriers upon photoexcitation. For instance, the degree of coupling between the charge carriers and phonons controls the charge-carrier mobility of the material. If the coupling is large enough, it will lead to strong charge–lattice interactions (i.e., small polaron formation or self-trapping charge). These interactions are most likely facilitated by the presence of Ag^+ and Bi^{3+} ions, high cation disorder, and layered ordering that reduces the electronic dimensionality of $\text{Cu}_2\text{AgBiI}_6$, making the localization of charge-carrier processes more likely to happen. Given that to some extent charge–lattice interactions could significantly affect the carrier mobility of the material, an accurate and detailed assessment of the strength of the interactions in $\text{Cu}_2\text{AgBiI}_6$ and the resulting charge-carrier mobilities is therefore of significant importance.

Herz and co-workers carefully address this issue by exploring and deciphering the nature of charge-carrier dynamics and the impact of the lattice on the carrier transport behavior of $\text{Cu}_2\text{AgBiI}_6$ with the aid of temperature-dependent photoluminescence, absorption, and optical-pump terahertz-probe spectroscopy. Time-resolved terahertz data clearly demonstrate that the ultrafast decrease in photoconductivity results in a localized charge carrier with a longer lifetime. The results also indicate that the carrier mobility of such a localized state increases as the temperature increases, providing clear evidence for the strong effect of the lattice on charge carriers in $\text{Cu}_2\text{AgBiI}_6$. Moreover, time-resolved data provide clear evidence not only for the formation of small-polaron or self-trapped charge within a picosecond time scale but also for the temperature-activated mobility of this polaron state. To assess and understand the charge mobility of $\text{Cu}_2\text{AgBiI}_6$ before and after the rapid localization of the charge carrier, the early-time transient decays are analyzed using a simple two-level model. Note that the authors assume in this model that photo-generated carriers are promoted into the conduction band as free charges (delocalized carriers) that are associated with a high mobility. This fast process is followed by a reduction in charge-carrier mobility due to the formation of the localized state where the charges return to the initial state.

In this Letter, the authors provide clear physical insight into how the lattice influences carrier transport in $\text{Cu}_2\text{AgBiI}_6$. More specifically, the authors clearly demonstrate that localized charge-carrier mobility could be controlled by temperature in $\text{Cu}_2\text{AgBiI}_6$, suggesting that extrinsic behaviors may still play an important role. This means that further enhancements in processing protocols can still significantly improve the mobility of charge carriers. The authors also observe that, while the existence of a self-trapped state and rapid carrier localization lowers charge-carrier transport to some extent, this influence is

not significant at device operational temperatures because the motion of small polarons is thermally activated. Finally, the authors conclude that a sufficiently activated carrier mobility with a low activation energy, a high absorption coefficient, a low exciton binding energy, and a long charge-carrier lifetime make this recently discovered lead-free material a very promising candidate for optoelectronic applications.

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Notes

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