



## Energy Focus

## Co-intercalation phenomena of Li in graphite anode improves Na-ion batteries

The possibility of replacing lithium with sodium in lithium-ion batteries (LIBs) is extremely attractive as sodium is cheap and abundant. However, graphite anodes, which are widely used in LIBs, perform very poorly in the sodium-ion battery (NIB). Birte Jache and Philipp Adelhelm of Justus-Liebig-University Giessen address this problem in their article in the September 15, 2014, issue of *Angewandte Chemie International Edition* (DOI: 10.1002/anie.201403734; p. 10169) and propose co-intercalation as a solution.

Sodium cannot be simply substituted for lithium in these batteries due to its larger ionic radius. A new approach is

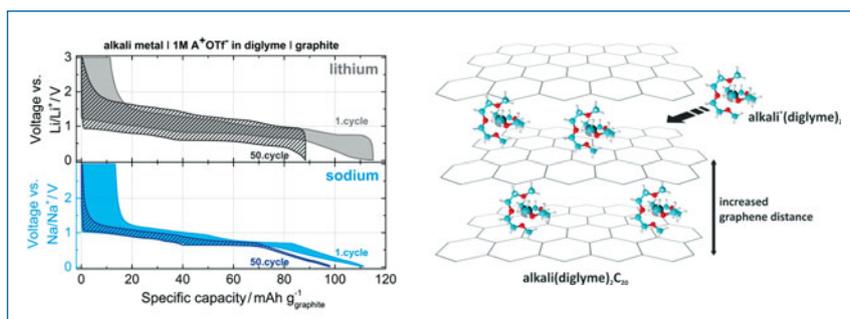
therefore required. In LIBs, lithium ions are reversibly intercalated (inserted) within layers of cathode or graphite anode. During discharge, the ions move from the anode to the cathode through an electrolyte, typically lithium hexafluorophosphate ( $\text{LiPF}_6$ ) in an organic solvent. They move back to the anode while charging. Graphite is successful as an anode in LIB because of its ability to reversibly intercalate lithium by forming a series of binary graphite intercalation compounds (*b*-GICs)  $\text{LiC}_x$  with the final stoichiometry  $\text{LiC}_6$ . Unlike other alkali metals, sodium does not form *b*-GICs under room temperature and pressure probably because of the mismatch between the graphite structure and the size of the Na ion. Hence, a different chemistry for a NIB is needed if graphite is to be retained as the anode.

Jache and Adelhelm make use of the fact that sodium can form ternary graphite intercalation compounds (*t*-GICs) to get around this problem. They use a single-solvent electrolyte based on diglyme and sodium triflate ( $\text{NaOTf}$ ) as the conductive salt. Sodium and solvent molecule co-intercalate graphite and a ternary compound,  $\text{Na}(\text{diglyme})_2\text{C}_{20}$  is formed, which exhibits favorable electrode properties. The size mismatch between the graphite lattice and the intercalant is small. The electrode reaction is characterized by high-energy efficiency, small irreversible loss during the first cycle, capacities close to 100 mAh/g for 1000 cycles, and coulomb efficiencies greater than 99.87%. These properties make NIB attractive for stationary applications. Importantly, this work can also inspire a search for better electrode reactions for NIBs since *t*-GICs are also formed with other solvents.

According to Takeshi Abe, a professor at Kyoto University, Japan, who did not participate in the study, the reversibility of the system is good and the electrode properties are very interesting. The volume expansion of the anode, however, is large and requires further study.

Many questions have to be answered scientifically before widespread applications can be developed for NIBs, and the present work points a way forward.

**N. Balasubramanian**



Specific capacities and charge/discharge characteristics of lithium/graphite and sodium/graphite cells cycled at 37.2 mA/g. The electrolyte is based on diglyme and lithium or sodium triflate.

## Energy Focus

## Thermoelectrics and effective medium theory—a recipe for innovation

Effective medium theory is typically employed to predict the macroscopic properties of multiphase composite materials, based on a knowledge of the properties of the individual components. Recently, however, a research team from the California Institute of Technology and the University of Southern California for the first time applied the theory to the opposite problem: calculating conductivity and mobility of individual

phases from the overall bulk properties of  $\text{Cu}_{1.97}\text{Ag}_{0.03}\text{Se}$ , a multiphase thermoelectric composite material.

Thermoelectric materials transform electricity into heat and vice versa. Compared to traditional heating and cooling systems, thermoelectrics can be used to heat or cool on a smaller or more localized scale (think “car seats”). In most cases thermoelectric materials possess a complex stoichiometry. Phase-pure syntheses can be challenging and the presence of impurity phases makes it difficult to accurately assess the properties of the thermoelectric target material.

Under the lead of G. Jeffrey Snyder, the researchers studied the multiphase composite  $\text{Cu}_{1.97}\text{Ag}_{0.03}\text{Se}$  with magnetic-field dependent resistivity measurements and analyzed the results using effective medium theory.

As recently reported in *Applied Physics Letters* (DOI: 10.1063/1.4897435), both the magnetoresistance and the Hall effect of the different phases within  $\text{Cu}_{1.97}\text{Ag}_{0.03}\text{Se}$  exhibit unique dependence on an applied magnetic field, which makes them identifiable to the researchers. One impurity phase, for example, exists at temperatures below 390 K and displays high mobility values, thereby dominating

the transport properties of the composite material despite taking up only 3% of the total sample volume.

“ $\text{Cu}_{1.97}\text{Ag}_{0.03}\text{Se}$  is a useful thermoelectric, which is intended to be used above the superionic phase transition temperature, at 390 K, where the material consists of a single phase,” said Snyder. “The research we carried out for this paper below the superionic phase transition temperature is more of an academic exercise, demonstrating that

we can determine the contributions of individual phases to bulk properties. It is really interesting to see how even a small impurity phase can dominate the overall behavior of a composite material.”

Understanding the contribution of individual phases to the overall properties of thermoelectric composite materials will guide researchers in their quest to optimize this class of materials and to further the implementation of thermoelectrics in everyday applications. The newly

discovered use of effective medium theory will certainly play an important role in future studies, as Tristan W. Day, who is the first author of this study, confirmed.

“What we have learned in this study, with regard to using effective medium theory in reverse, is useful for studying other composite materials as well. The methodology can be applied to our work on organic/inorganic thermoelectrics, for example,” said Day.

**Birgit Schwenzer**

### Energy Focus

#### Insulator triggered charge balance for high-performance QLEDs

Vacuum deposition is the primary technique currently employed by industry for producing commercial light-emitting diodes (LEDs) as their performance is superior to that of solution-processed LEDs. However, a team of nine scientists from China led by Yizheng Jin and Xiaogang Peng at Zhejiang University have recently taken an important step forward in the development of solution-processed LEDs, as reported in the November 6, 2014, issue of *Nature* (DOI:10.1038/nature13829; p. 96). The research team achieved this by using nonblinking quantum dots (QDs) with a photoluminescence quantum yield above 90%. As Peng explained, “Blinking quantum dots are simply not

well-suited for the development of highly efficient LEDs.”

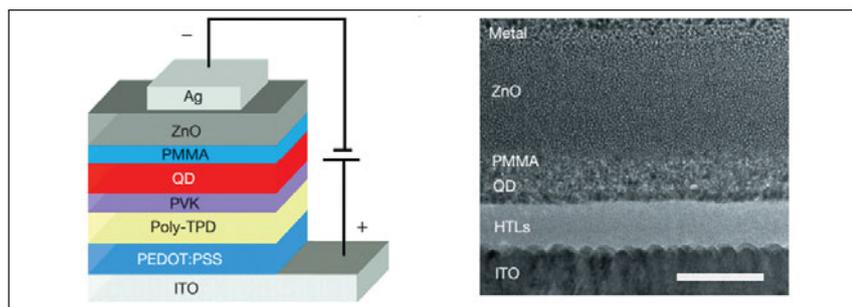
Previous solution-processed LEDs have suffered from several performance deficiencies, including high turn-on voltages, low power efficiency, short lifetimes, and significant roll-off. According to Peng, “An LED with significant roll-off is not useful for many applications, because they are less efficient when operated at high current densities.”

The deep-red LED designed by Peng, Jin, and their colleagues is an eight-layer device, as shown in the accompanying figure. The device has a low turn-on voltage and high power efficiency because of the highly efficient injection of holes into the QD layer from the bilayer located underneath. Meanwhile, ZnO nanocrystals are deposited above the QD layer to act as electron-transport interlayers, because they enable high electron mobility.

The layer of PMMA between the QD and ZnO layers was found to be extremely important, because it acts as an insulator. When the PMMA layer is absent, excess electron current is injected into the QD layer, resulting in poor stability, a reduction in performance, and a 50% reduction in the initial luminance within 10 hours when operated at  $6600 \text{ cd m}^{-2}$ . To put this in perspective, Jin said that “indoor lighting [white light] requires a brightness of roughly  $5000 \text{ cd m}^{-2}$  while displays range from 100 to  $1000 \text{ cd m}^{-2}$ .” When a thin PMMA layer is deposited into the device, the half lifetime for the initial luminance is increased to 95 hours when operated at  $10,600 \text{ cd m}^{-2}$ . Based on this finding, it is predicted that the half lifetime of this same device would be over 100,000 hours if operated at  $100 \text{ cd m}^{-2}$ . Most importantly, the device with the PMMA layer is easily reproducible and yields high performance that is very comparable to vacuum-deposited organic LEDs.

This initial work relied on QDs with an emission band in the deep-red region. However, the researchers see no fundamental difficulties that would preclude them from using QDs with other emission bands. In fact, they are already testing the system with other colors, because, as Peng explained, “In today’s energy-sensitive society, high-performance LEDs fabricated with inexpensive techniques might play a critical role in multiple industrial sectors, such as displays and lighting.”

**Anthony S. Stender**



Transmission electron micrograph (right) shows the structure of the high-performance light-emitting diode (LED) that incorporates nonblinking quantum dots; scale bar = 100 nm. The eight layers consist of indium tin oxide (ITO), poly(ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), poly(*N,N'*-bis(4-butylphenyl)-*N,N'*-bis(phenyl)-benzidine) (Poly-TPD), poly(9-vinylcarbazole) (PVK), CdSe-CdS core-shell quantum dots (QDs), ZnO nanoparticles, and silver (Ag). Reproduced with permission from *Nature* **515** (7525) (2014), DOI: 10.1038/nature13829; p. 96. © 2014 Macmillan Publishers Ltd.