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 ($LiPF_6$) 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) Li Cx with the final stoichiometry 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 (NaOTf) as the conductive salt. Sodium and solvent molecule co-intercalate graphite and a ternary compound, Na $(diglyme)_2$ 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.

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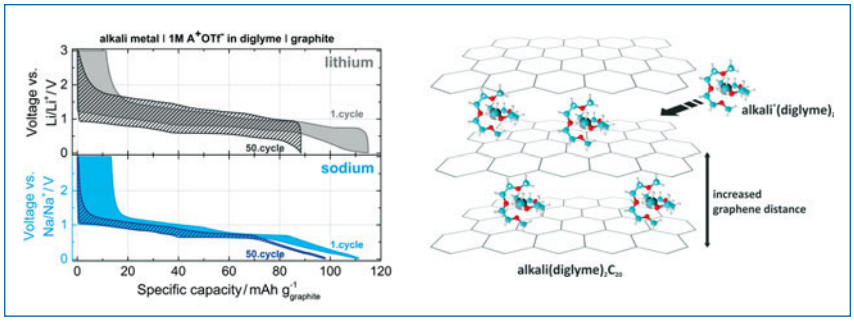

Specific capacities and charge/discharge characteristics of lithium/graphite and sodium/graphite cells cycled at 37.2 mA/g. The electrolyte is based on diglyme and lithium or sodium triflate.

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 $Cu_{1.97}Ag_{0.03}Se$, 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 $Cu_{1.97}Ag_{0.03}Se$ 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 $Cu_{1.97}Ag_{0.03}Se$ 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