



to 230°C. The migration of oxygen ions was demonstrated to be significantly promoted by the application of an electric field through the film thickness. Furthermore, the researchers found that the process of cobalt oxidation and oxygen migration was semi-reversible. By simply reversing the polarity of the field, oxygen at the  $\text{GdO}_x/\text{Co}$  interface returned to the oxide layers, but the oxygen buried deeper in the Co layer remained in place.

The researchers asserted that the films must be broken up into individual grains acting as if isolated, rather than as a continuous

film. Oxygen that is loosely bound to the surface of the oxide grains can be pulled away much easier and diffuse readily along the surface of the Co grains. However, diffusion would be somewhat slower into the core of the Co grains producing a slow transition from a metallic to insulating state with an accompanying change in the magnetic properties. When the field is reversed the oxygen on the surface of the Co grains can diffuse back to the oxide layer, but due to an electric screening effect, the oxygen in the core of the Co grains remains trapped. This remaining oxide acts as a secondary

magnetic phase and an irreversible change in the overall magnetic properties.

Until now this effect has only been seen in ultrathin films; this new work points to its application in bulk materials. Using this reversible migration of ions as a way to control physical properties in materials holds enormous potential for improving the energy efficiency of countless types of devices. Gilbert envisions this process enabling “control over essentially every physical property of our material ... this work is just the first step.”

**Ian McDonald**

### Energy Focus

#### Novel method developed to investigate stiffness and mechanical stress in Li-ion batteries

Researchers typically gauge the safety and reliability of batteries by the amount of heat that they evolve and the number of cycles that they can sustain before degrading. In addition, in Li-ion batteries, the ion intercalation charge-discharge process used also induces mechanical stress and strain in the electrode materials. The resulting deformation and delamination may, over

time, lead to device failure. Due to the complex, heterogeneous nature of the lithium-ion exchange and the structures of the composite electrode materials used, it has proven challenging to develop effective techniques for assessing the kinetic effects of stress and strain, and correlating them with device charging and discharging.

Now Hadi Tavassol, Elizabeth M.C. Jones, Nancy R. Sottos, and Andrew A. Gewirth of the University of Illinois at Urbana-Champaign (UIUC) have developed a novel approach that assesses *in situ* electrochemical stiffness of graphite-lithium intercalation compounds during cycling. They combined *in situ* electrochemical and mechanical measurement techniques to measure the intercalation-induced stress and strain of a graphite anode. The researchers used galvanostatic cycling and cyclic voltammetry, respectively, to assess the effects of capacity and electrochemical potential fluctuations on lithiation. The results are reported in a recent issue of *Nature Materials* (doi:10.1038/nmat4708).

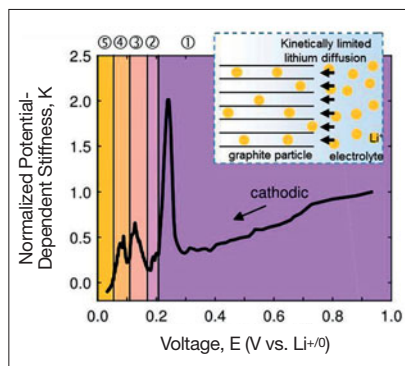
Gewirth, in the Department of Chemistry, says, “For the first time we were able to correlate stress with strain during the lithiation event. Our finding that the two are asynchronous has important consequences for understanding and controlling battery behavior during charge and discharge.” Sottos, of the Department of Materials Science and Engineering, adds, “We are beginning to understand some of the factors that

hinder faster battery charging. These experiments provide insight that it’s not just an electrochemical issue; the coupling to mechanics is also important.”

This unique *in situ* electrochemical stiffness measurement has already provided important information about the complex mechanical dynamical responses of electrodes during charging and discharging. In particular, a lithium-ion concentration gradient appears to be one of the biggest sources of stress on anodes. Kinetically limited lithium diffusion is less significant during slow charging but becomes a major stress factor during rapid cycling, and scales with the rate of charging. Ion insertion into the structure and the repulsion of nearby layers also act as additional sources of stress. In contrast, mechanical strain and material expansion strongly depend on ion intercalation and directly increase with slower charge rates. Unlike stress, electrochemically driven strain depends predominantly on the total capacity (i.e., stored charge) of the electrodes.

This research provides insight into the electromechanical coupling behavior of electrodes under their expected operating conditions. While certain energy-storage systems demand high charge and discharge rates, other uses prefer higher specific energy densities. Such a comprehensive *in situ* technique is vital for efforts to evaluate novel battery electrode materials and select compositions that are well tailored for specific applications.

**Boris Dyatkin**



Electrochemical stiffness changes during lithiation of a composite graphite electrode. As lithium ions intercalate into the graphite anode during a multistage process, they influence the mechanical properties of the electrode. The charging process generates unique stage-dependent stress and strain in the graphite-lithium intercalation compound. Credit: Hadi Tavassol, Elizabeth M.C. Jones, Nancy R. Sottos, and Andrew A. Gewirth.