Electrochemical Properties of Copper Hydroxysulfate Mineral Brochantite Upon Reaction with Lithium

Ran Zhao,[a] Ting Yang, [b] and Candace K. Chan*[b]

[a] Department of Chemistry and Biochemistry,
Arizona State University, Tempe, AZ
[b] Materials Science & Engineering
School for Engineering of Matter, Transport and Energy
Arizona State University, Tempe, AZ

Owing to its high energy density and light weight, Li-ion batteries have taken away over half of the worldwide rechargeable battery market. Cathodes for Li-ion batteries have been under investigation since the commercialization of Li-ion batteries in 1991. Recent progress in nanostructured negative electrode materials has resulted in significantly improved capacities, which demand higher capacity cathodes to match.

Recently, there has been much interest in polyanion and mixed anion materials such as LiFeSO4F and LiFePO4(OH). The advantage of mixed anion materials is that the electrode potential can be tuned by the induction effect and different environments for Li+ insertion may exist. Furthermore, many metal hydroxysulfate and hydroxyphosphate materials, of the form Mx(OH)y(XO4)n, occur naturally as minerals with M = Cu, Fe, and Mn. They come in a variety of expanded frameworks, tunnel, and layered structures and may be interesting candidates for electrode materials in Li-ion batteries.

In this work, Cu4(OH)6SO4 (brochantite), which has a layered structure, is studied as a cathode material of Li-ion battery. First, brochantite was synthesized using two methods, titration and hydrothermal, to produce different particle sizes and morphologies. Next, the samples were tested in half-cells with Li metal for lithiation/delithiation. Capacities >400 mAh/g were observed for brochantite with nanoplate morphology. The brochantite samples were characterized using ex-situ X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, and transmission electron microcopy in order to identify the morphological and structural changes occurring during the electrochemical reactions, and also to determine if the reaction mechanism is a conventional intercalation or conversion reaction. The fundamental knowledge gained from these studies can be applied to better understanding of the electrochemical properties other mixed anion materials.