

## Designing Porous Electrodes for Li-ion Batteries

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In the past 10 years considerable effort has been made to develop Li-ion battery materials for electric and hybrid-electric vehicles. While considerable improvements have been made, lower cost electrodes with higher energy or power density are still needed. One of the most popular ways to improve the power density, and sometimes energy density, is by synthesizing nanoparticles of the desired materials. Multidimensional porous electrodes in Li-ion batteries offer many of the same advantages observed from nanoscaling electrode materials, such as shorter solid state diffusion lengths and higher Li-ion fluxes, while also providing more consistent interfacial contact with the carbon and binder due to the larger particle sizes. While the porous electrodes do lower the volumetric energy density compared to a solid micron sized particle, when compared to nanoparticles the porous electrodes can have a higher tap density, offsetting some of the energy density losses. Since the nanoporous electrodes are better suited to maintain contact with the binder and conductive carbon as the electrode volume changes from the storage or release of Li-ions, we believe these types of materials are a viable method to significantly improve battery recharge times. If a Li-ion battery electric vehicle could recharge in minutes instead of hours consumer concerns about range anxiety could be addressed. In some exceptional cases the nanoscaling that occurs to make porous electrodes has been shown to “activate” a material for energy storage. A great example studied by one of the authors is  $\beta$ -MnO<sub>2</sub>, which becomes electrochemically active if nanocast in mesoporous silica such as KIT-6.<sup>1</sup> This presentation will highlight our labs continued efforts to synthesize and study porous oxide, sulfide, and phosphate electrodes for Li-ion batteries.

To make our oxide and sulfide electrodes we principally rely on hard templating within KIT-6 silica so a uniform, 3-D pore structure is obtained for investigation. Once the electrode materials are prepared we perform a variety of structural and electrochemical characterization tests pre and, if warranted, post electrochemical testing. Since the KIT-6 templated electrodes have a 3-D mesostructure, we can verify if the energy storage mechanism destroys the pore structure and/or crystallinity of the material during cycling. Generally we limit the metals studied to Fe, Mn, Co, Ni and Cu because of their relative abundance and manageable material cost. While oxide electrodes have been significantly studied in the past, less work has been done for porous sulfur materials. Sulfur, being very abundant and low cost, is worthy of investigation for rechargeable Li-ion batteries. In fact, some primary Li-ion batteries are based upon these metal sulfur electrodes. One of the principle differences between many oxide and sulfide compounds is the oxidation state of the metal. In oxides the charge balance for the O<sup>2-</sup> anions comes from the metal cations changing oxidation state, but in sulfide materials the sulfur can adopt multiple oxidation states. Generally the higher transition metal oxidation states are needed for cathode electrodes because they result in higher cell voltages. However, the ability of sulfur to change its oxidation state results in materials that may be able to store multiple lithium ions per transition metal,

resulting in higher capacities that offset the energy losses from lower operating voltages.

Recognizing some of the difficulties in creating lithiated nanocast electrodes, we have also begun to look at other ways to make porous materials. An interesting approach is to adopt zeotype framework structures, which we are currently investigating via ionothermal synthesis. Ideally these zeotype electrodes will be microporous to give good volumetric energy density, have multidimensional channels for ion diffusion, and will be robust to oxidation state changes. To start we are targeting phosphate materials because the tetrahedral PO<sub>4</sub><sup>3-</sup> is commonly observed in ALPO zeolites. In a recent paper we demonstrated our ability to make Fe, Mn, and Co phosphate frameworks by using deep-eutectic solvent ionothermal synthesis.<sup>2</sup> This paper represented a very important first step in designing zeotype cathodes because it demonstrates that Fe, Mn, and Co will adopt the tetrahedral sites necessary to build the frameworks. In addition, changing the synthesis parameters allowed us some control over the dimensionality and ring size, which will allow us to optimize the electrode for maximum performance. As an example, when using the deep-eutectic solvent of choline chloride and N,N'-dimethylurea we observed cobalt phosphate structures that would phase change to different structures as reaction time increased. At short reaction times a layered cobalt phosphate structure (DEL-1) was collected, which phase changes into a 3-D framework (DEL-2), which will then transform into a 2-D framework (CoPO<sub>4</sub>-ABW) that will finally phase change to a 1-D channel structure (CoPO<sub>4</sub>-HEX) if the synthesis temperature is high enough. The next big challenge for these types of materials—a task our lab is currently engaged in solving—is how to exchange or directly template Li-ions into the multidimensional framework structures.

1. F. Jiao and P. G. Bruce, *Advanced Materials*, **19**, 657-660 (2007).
2. B. Yonemoto, Z. Lin, and F. Jiao, *Chemical Communications*, **73**, 9132-9134 (2012).