Synthesis and Intercalation Properties of Nanostructured Amrophous Manganese Oxide and Lithium Manganese Oxide Cryogels

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In recent years, amorphous manganese oxides have received increasing attention as high-capacity intercalation cathodes for rechargeable lithium batteries [1-4]. Most of these materials are produced via redox synthesis routes in aqueous or non-aqueous solutions to directly yield powders. Compared with these methods, sol-gel synthesis and processing of manganese oxides via a hydrogel offers an attractive route, one characterized by homogeneous mixing of reactants at the molecular level, precise control over the cationic composition, good control over morphology of the resulting phases including ease for creating nanostructured morphology, and convenience for thin film fabrication [5-8]. In this contribution, we report sol-gel synthesis and processing of nanostructured amorphous manganese oxide and lithium manganese oxide cryogels derived from monolithic hydrogels, their superior lithium intercalation properties, as well as surprising findings from the study that electrochemically inactive compounds may become active once their long-range-order structure is reduced to short-range-order.

Our first motivation of the study is to design an amorphous manganese (IV) dioxide with a nanostructured architecture. Such a material would combine the advantage of the amorphous structure, which leads to high intercalation capacity, and that of nanostructured architecture, which leads to high rate capability. This is achieved by forming a monolithic Mn (IV) oxide hydrogel and subsequently removing the water in the hydrogel by freeze-drying. The freeze-drying process largely preserves the amorphous structure of the oxide and its nanostructured architecture inherent in the hydrogel. The resultant manganese dioxide cryogel is shown to be indeed X-ray amorphous and possessed of a nanostructured architecture with a BET surface area as high as 350 m^2/g. The material exhibits specific capacities of 289, 217 and 174 mAh/g at C/100, C/5 and 2C rates, respectively, demonstrating simultaneously high capacity and excellent rate capability. A specific capacity of 174 mAh/g at 2C rate appears to be the highest capacity at such a high rate among different kinds of manganese dioxides reported.

The monolithic hydrogel to cryogel route allows precise control of the cationic composition of the resulting oxides. This enabled us to synthesize lithium-rich manganese (IV) oxide cryogels and investigate the effect of the lithium content on intercalation properties. The lithium-rich manganese (IV) oxide cryogels were obtained by freeze-drying the hydrogel followed by heat treatment at 400 ºC. Although not as amorphous as the manganese oxide cryogels obtained by freeze-drying without any subsequent heat treatment, these compounds show very broad X-ray diffraction peaks and their structure may be characterized as largely amorphous or short-range-order. It was found that the cycling stability of the lithium manganese (IV) oxide cryogels clearly improves with increasing lithium content. For a Li/Mn ratio equal to 2, the cryogel possesses a short-range-order structure bearing similarity to that of Li_2MnO_3 of the rock-salt type structure. While the crystalline rock-salt Li_2MnO_3 is electrochemically inactive, the short-range-order Li_2MnO_3 exhibits a surprising lithium intercalation capacity around 160 mAh/g and excellent cycling performance, raising intriguing mechanistic questions while suggesting unique advantages associated with intercalation materials of short-range-order structures.

References

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