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Tunnel Manganese Oxides for Energy and Water Treatment Applications

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Abstract

Energy storage and the production of fresh water are essential technologies to develop as our demand for portable power and utilization of limited freshwater resources grow. Large-scale solutions to growing energy and water concerns based on electrochemical systems require the utilization of inexpensive and environmentally friendly materials. Tunnel manganese oxides (TuMOs) are attractive candidates for such systems due to their intrinsic low cost, low toxicity, and high electrochemical activity. These materials are built from corner and edge sharing MnO_6 octahedra arranged around stabilizing ions and water molecules to form structural tunnels, which provide one-dimensional (1D) diffusion channels for ion intercalation. Tuning synthesis parameters allows for control of the size and shape of the structural tunnels through

incorporation of templating ions into the precursor mixture, and thus, the TuMO system provides a unique platform to investigate the relationship between the size/ionic content of 1D diffusion channels and electrochemical performance in systems containing ions of different sizes. This thesis is focused on utilizing TuMOs synthesized with nanowire morphology that display a controlled variation of tunnel size and shape in energy and water treatment applications to understand the effect of tunnel dimensions and ion content on their functional properties. Specifically, the TuMO nanowires are investigated as active materials for electrodes in nonaqueous Li-ion and Na-ion batteries and in a water desalination technique termed hybrid capacitive deionization (HCDI).

In battery systems with electrochemically cycled ions of different sizes, the effects of both tunnel size and ionic content on electrochemical performance are studied. At lower current rates, TuMOs with larger tunnels and lower ionic content exhibit higher capacities. At higher current rates, TuMOs containing Na^+ ions in the tunnels show better rate capability in Na-ion cells containing larger electrochemically cycled Na^+ ions than in Li-ion cells containing smaller electrochemically cycled Li^+ ions, implying that crystallographically well-defined intercalation sites created via chemical incorporation

of stabilizing ions play an important role in the performance of TuMO electrodes. Capacity fade over extended cycling is identified as a major performance limitation of TuMO electrodes, and this is overcome by successfully applying a chemical modification strategy consisting of the introduction of a small fraction of stabilizing molecules into the structural tunnels.

Additionally, TuMOs are for the first time evaluated as Faradaic electrodes in HCDI cells. They demonstrate high ion removal capacities and ion removal rates, as well as stable cycling behavior, in NaCl, KCl, and $MgCl_2$ solutions. It is found that the ion removal capacity of a given TuMO phase depends on the relationship between the hydrated radii of the ion removed from solution and the size of the structural tunnels in the TuMO, with materials containing larger structural tunnels showing improved removal of ions with larger hydrated radii. Further, it is determined that the mechanism by which ions are removed from solution is based on both surface adsorption and intercalation of ions into the structural tunnels. Ultimately, this thesis shows that by understanding the relationship between ion size and host crystal structure, chemical modification of tunnel content, and the mechanism between active electrode material and ions in solution, the performance of materials with 1D diffusion

pathways in applications based on ion insertion/deinsertion can be maximized. Moreover, a basis for the selection of TuMOs for future electrochemical applications is provided.