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Mass Transport Properties of Manganese Dioxide Phases for Use in Electrochemical Capacitors: Structural Effects on Solid State Diffusion

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Manganese dioxide is a promising electrode material for use in supercapacitors. It exhibits relatively high capacitance due to pseudo-capacitance, which is the result of fast, reversible faradaic reactions occurring in conjunction with double layer charging. For manganese dioxide, pseudo-capacitance arises when a proton (or cation) from the solution combines with an electron and diffuses through the manganese dioxide structure.

The rate of solid state diffusion is expected to have an influence on the capacitive performance of the material; i.e., if the proton can diffuse quickly into the bulk, this could increase the amount of charge stored and improve charge/discharge capabilities. However, the rate of diffusion can be affected by the structure of the material. In this work, the solid state mass transport characteristics of various manganese dioxide phases has been examined.

The phases examined included γ-MnO_2 (electrolytic manganese dioxide), β-MnO_2 (pyrolusite), ramsdellite, δ-MnO_2 (birnessite), α-MnO_2 (cryptomelane) and λ-MnO_2. Diffusion within each phase was examined using electrochemical impedance spectroscopy (EIS) and step potential electrochemical spectroscopy (SPECS).

$A\sqrt{D}$ (where A is surface area and D is the diffusion coefficient) decreases with depth of discharge, and is also affected by the phase of manganese dioxide studied, with γ-MnO_2 exhibiting the highest $A\sqrt{D}$ value. Overall, values of $A\sqrt{D}$ varied between $3\times10^{-8} – 2\times10^{-10}$ $m^3/s^{1/2}/g$, which is comparable with literature data.

These results also provide information on the kinetics of lattice expansion and contraction which occur during cycling. High surface area phases such as γ-MnO_2, ramsdellite and cryptomelane, showed significant hysteresis in lattice contraction which is attributed to the diffusion of protons through surface domains. Low surface area phases (pyrolusite and λ-MnO_2) did not display this hysteresis, suggesting that proton diffusion occurs predominantly in the bulk of the material.

No direct correlation between mass transport and specific capacitance is observed, suggesting that other material properties contribute to specific capacitance.