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Investigations of Pseudocapacitance Mechanisms of MnO_x-Coated Carbon Nanofoams

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Carbon nanofoams are a class of free-standing electrode architectures with controllable macroscale dimensions (both in area and thickness) and nanoscale dimensions (pore sizes from 10-200 nm). Coating these carbon nanofoams with transition metal oxides such as MnO_x increases the charge-storage capacity via pseudocapacitance. Some debate still surrounds the charge-compensation mechanism for MnO_x with the majority of the literature for thin films showing cations (either in the form of electrolyte cation or protons) are responsible for charge-compensation during oxidation and reduction when cycled in mild aqueous electrolytes.

The electrochemical quartz crystal microbalance has traditionally been used for studying acoustically thin (rigid) films of materials, allowing for determination of mass changes for electrodes (or their corresponding films) under electrochemical cycling. New developments in electrochemical quartz crystal microbalance methods has led to the ability to study charge-compensation mechanisms in-situ for new classes of electrode architectures such as carbon nanofoams and power-composite electrodes used in electrochemical capacitors.

Birnessite-type MnO_x-coated carbon nanofoams, cycled in mild aqueous electrolytes such as 2.5 M LiNO₃, NaNO₃, KNO₃, Li₂SO₄, or Na₂SO₄ reveal that, unlike thin films, anions are primarily responsible for charge-compensation mechanism. In restricted environments (pores < 40 nm), depletion effects are observed where a switch in the charge-compensation mechanism takes place between NO₃⁻ and Li⁺. Electrochemical cycling of spinel MnO_x in 2.5 M LiNO₃ or Li₂SO₄, reveals two peaks associated with Li⁺ insertion. Switching the electrolyte from LiNO₃ to NaNO₃, produces an overall increase in mass and decrease in peak current, owing to the replacement of Li⁺ with Na⁺ at active sites.

Keywords: pseudocapacitance; MnO_x; electrochemical quartz crystal microbalance