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Cycle Behavior of Aqueous and Nonaqueous Vanadium Oxide Electrochemical Capacitors

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Electrochemical capacitors (ECs) are an important class of energy storage because they provide higher energy densities than traditional electrostatic capacitors and higher power densities than battery systems.[1,2] They are further distinguished by the two primary charge storage mechanisms that dominate these devices. The first, the electrochemical double layer capacitor, stores charge electrostatically across the double layer that forms at the electrode/electrolyte interface and ideally no Faradaic charge transfer occurs across the interface, which is unlike the second type of device, the pseudocapacitor. A pseudocapacitive EC primarily stores charge indirectly by highly reversible redox reactions at the surface and in the bulk of the material, i.e. the transition between the various oxidation states in transition metal oxides accompanied by the intercalation and deintercalation of electrolyte ions. ECs are regarded for their high specific power and energy density, low material cost and toxicity as well as a long cycle life owing to high reversibility.[1-3]

The study of transition metal oxides for utilization in electrochemical capacitors began with the discovery of the capacitive properties of hydrated ruthenium oxide,[4] but in 1999, Lee and Goodenough were the first to describe vanadium oxide as a more cost-effective material for electrochemical capacitors.[5] Vanadium oxide is a desirable active material due to its wide range of stable oxidation states (V, IV, III and II) and its relatively low cost and toxicity compared to RuO_2.[5,6] The initial capacitive properties and degradation mechanisms for electrodeposited vanadium oxide were previously studied in a variety of pH environments using aqueous KCl electrolyte solutions.[7]

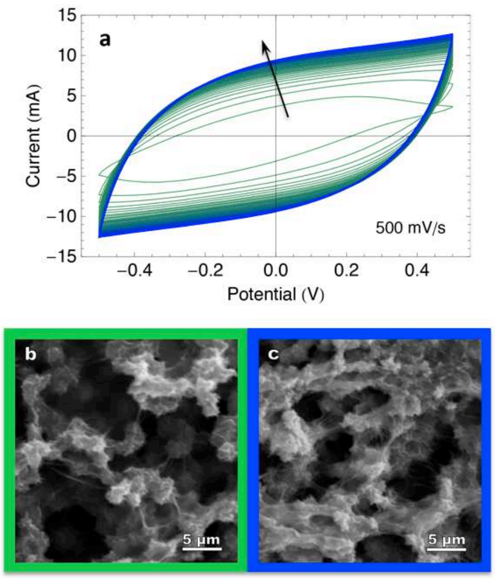

Figure 1: Cycle behavior of a symmetric vanadium oxide EC with an agar gel electrolyte made from 3.0 M NaCl at pH 3.0 cycled at 500 mV/s for 50,000 cycles a) plotted every 500 cycles (the arrow indicating the shape-change with increased cycling) as well as the morphology b) before and c) after cycling.

In the current study, the initial capacitance, electrochemical impedance and cycle behavior of symmetric vanadium oxide ECs are studied for both aqueous and nonaqueous electrolyte-solvent systems. An aqueous system utilizing a 3.0 M NaCl electrolyte at pH 3.0 cycled at 10 mV/s exhibits an excellent 96% capacitance retention over 3000 cycles. An equivalent system tested at 500 mV/s displays an increase in capacitance over the first several thousands of cycles, and eventually stabilizes over 50,000 cycles (See Figure 1). Electrodes cycled in nonaqueous 1.0 M LiBr in PC exhibit mostly non-capacitive charge-storage over the first 1000 cycles at 10 mV/s but eventually stabilize to a mostly capacitive charge-storage mechanism tested up to 2000 cycles (See Figure 2). Furthermore, electrodes cycled in DMSO exhibit a gradual capacitive decay over 10,000 cycles at 500 mV/s. Morphological analyses and electrochemical impedance modeling are utilized to explain the observed cycle behavior.

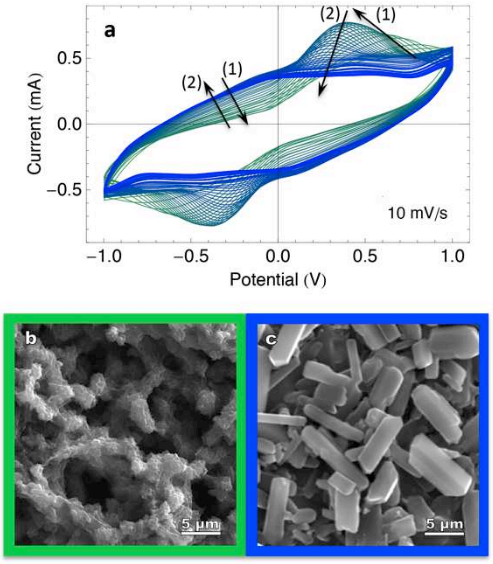

Figure 2: Cycle behavior of a symmetric vanadium oxide EC with a nonaqueous 1.0 M LiBr in DMSO electrolyte at 10 mV/s for 2000 cycles a) plotted every 40 cycles (the arrows indicating the shape-change with increased cycling) as well as the morphology b) before and c) after cycling.

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