Electrochemical Capacitors with KCl Electrolyte

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A need to meet the intermittent power demands placed on an electrochemical power source has stimulated interest in hybrid electrical devices in which an electrochemical capacitor complements a secondary battery [1]. Electrochemical capacitors that have been investigated for this purpose include carbon compounds [2,3] having an electrochemical double layer that is charged by a *charging current* and metal oxides [4,5] that have a large faradaic capacitance (pseudo-capacitance) that is charged by a *faradaic current*. In particular, the amorphous hydrate $RuOOH \cdot nH_2O$ obtained from RuO_2 has attracted considerable attention as it shows a high capacity of over 700 F/g and an excellent cyclability [6]; but RuO_2 is too expensive to be commercially attractive. Therefore, there is a growing interest in identifying a less expensive oxide that can provide an equivalent performance. The phosphopolymolybdate $H_3PMo_{12}O_{40} \cdot nH_2O$ is a possible alternative as it is stable in contact with an acidic NAFION membrane and has all its Mo atoms at the surface of an individual Keggin unit; but the capacity of this compound was found to be limited to one proton for three Mo atoms [7].

The search for alternate metal oxides has previously been narrowed by the assumption that a large faradaic capacitance and fast discharge are only to be associated with the chemisorption and desorption of protons on an oxide surface in an aqueous electrolyte. This assumption has led to the choice of concentrated sulfuric acid as the electrolyte [8,9]. A hydrated oxide and a strong-acid electrolyte would enhance the capacity and the speed of discharge since the proton has access to inner surfaces not readily reached by alkali ions, and protonic conductivity in a concentrated acid solution has a high ionic conductivity. However, most metal oxides dissolve over time, if not immediately, in a strong acid medium. Moreover, strong acids are corrosive of the metal alloys that might be chosen for the current collectors. Finally, strong acids are an environmental hazard.

In order to circumvent the strong-acid problem, we have explored the use of a KCl aqueous solution as the electrolyte for a faradaic electrochemical capacitor. Although it has a lower conductivity than a concentrated acid, an aqueous KCl solution is used widely as a supporting electrolyte in the field of electrochemistry as it has a relatively high K^+-ion conductivity; the K^+ ion has a smaller hydration sphere than either Na^+ or Li^+. We show below that K^+ is the working ion in our system, which indicates that the realization of a large faradaic capacitance is not restricted to the chemisorption and desorption of protons. In our investigation, the use of K+ as the working ion in a faradaic electrochemical capacitor requires an oxide morphology that allows access to internal surfaces of oxide aggregates by the K^+ ions. We therefore chose to investigate first hydrated potassium manganese dioxide, $K_xMnO_{2+\delta} \cdot nH_2O$. This

oxide has a layered structure with a large enough interlayer separation for the insertion of additional K^+ ions between the MnO_6 layers. Moreover, the oxide is easily synthesized and has a much lower cost than RuO_2. However, it is necessary to distinguish the use of this electrode material in a faradaic electrochemical capacitor from its use as a cathode in a rechargeable battery. To date, $K_xMnO_{2+\delta} \cdot nH_2O$ has only been evaluated as a battery cathode [10-12].

In the course of this work, it became apparent that the capacity of the electrode increased with the fraction of amorphous material. Therefore, we chose next to investigate amorphous $MnO_2 \cdot 0.93H_2O$ and amorphous $V_2O_5 \cdot nH_2O$, which is much simpler to prepare in a completely amorphous state. With this material, we demonstrate electrochemical capacitor performance with a comparable capacity to that of $K_xMnO_{2+\delta} \cdot nH_2O$.

Potassium manganese dioxide $K_xMnO_{2+\delta} \cdot nH_2O$, amorphous $MnO_2 \cdot 0.93H_2O$ and amorphous $V_2O_5.nH_2O$ in a mild 2 M KCl aqueous electrolyte with controlled conditions prove to be excellent electrodes for faradaic electrochemical capacitors. The $K_xMnO_{2+\delta} \cdot nH_2O$ materials were prepared by direct thermal decomposition of $KMnO_4$ and contained a large amorphous / crystalline ratio. A sample decomposed at 550 °C gave a specific cyclic capacitance between -0.2 and +1.0 V vs SCE of 240 F/g, which corresponds to nearly one-third of the Mn(IV) ions participating in the faradaic reaction. Excellent cyclability at 2 mA/cm^2 was found for 100 cycles. On short-circuit, $K_{0.31}MnO_{2.12} \cdot 0.63H_2O$ in 2 M KCl and pH 10.6 aqueous solution gave an initial current density of 0.58 A/cm^2 and a total released charge of 4.6 C/cm^2 compared with 0.32 A/cm^2 and 11.1 C/cm^2 for $RuOOH \cdot nH_2O$ in 5.3 M H_2SO_4. Similar results obtained with amorphous $MnO_2 \cdot 0.93H_2O$ demonstrate that alkali ions can be used as the working ion in a faradaic electrochemical capacitor, which frees the search for new materials from the constraint of working in a strong-acid aqueous medium.

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