

BRIEF COMMUNICATION

Supercapacitor Behavior with KCl Electrolyte

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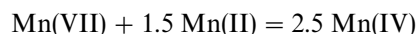
Received November 24, 1998; accepted December 7, 1998

Amorphous $\text{MnO}_2 \cdot n\text{H}_2\text{O}$ in a mild 2 M KCl aqueous electrolyte proves to be an excellent electrode for a faradaic electrochemical capacitor cycled between -0.2 and $+1.0$ V versus SCE. In this potential range, it had ideal behavior with a specific capacitance of *ca.* 200 F/g, excellent cyclability at 2 mA/cm² over 100 cycles, and a short-circuit initial current density of 0.23 A/cm² with a total released charge of 3.8 C/cm² as compared to 0.32 A/cm² and 11.1 C/cm² for $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ in 5.3 M H_2SO_4 . © 1999 Academic Press

Electrochemical capacitors are of interest for auxiliary energy storage in hybrid electrical devices powered by a rechargeable battery (1). An electrochemical double-layer capacitor (EDLC) uses the physical separation of electronic charge in the electrode and ions of the electrolyte adsorbed at the surface (2). These capacitors have a lower specific capacitance than an optimal faradaic supercapacitor that is charged by chemisorption of a working cation of the electrolyte at a reduced complex at the surface of the electrode (3). Amorphous, hydrated ruthenium oxide, $\text{RuO}_2 \cdot n\text{H}_2\text{O}$, in strong acid, for example, is capable of chemisorbing one proton per Ru atom to give a capacity of 700 F/g and an excellent cyclability (4). Although this performance is optimal, $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ is considered too expensive to be commercially attractive, which has invited a search for alternate materials (5). Since the small size of the proton offers the best chance to achieve optimal chemisorption, the search has been restricted to materials stable in strong acids. The choice of strong-acid electrolyte was reinforced by the belief that the speed of discharge would be governed by the mobility of the working ion in the electrolyte (6). Unfortunately, most candidate electrode materials are unstable in strong acid; it was even necessary to use a proton exchange membrane for $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, and this electrode accepts only one proton for every three Mo atoms (5). In this

paper we demonstrate that a mild potassium-chloride (KCl) aqueous electrolyte can be used for a faradaic capacitor giving a comparable discharge rate to that of amorphous $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ in 5.3 M H_2SO_4 , but the larger K^+ ion appears to limit the capacity to chemisorption of a single K^+ ion per three electrode cations.

For the electrode, we used amorphous, hydrated manganese dioxide, $a\text{-MnO}_2 \cdot n\text{H}_2\text{O}$, that was prepared by mixing 1.58 g of KMnO_4 dissolved in 60 ml of deionized water with 3.68 g of manganese(II) acetate dissolved in 100 ml of deionized water. The reaction



was carried out for 6 h under constant stirring of the solution. The dark brown precipitate was filtered with a ceramic filter, washed several times with deionized water, and then conventionally dried at 110°C for 12 h. The amorphous character of the product was confirmed with a Philips powder X-ray diffractometer and the BET surface area of the dried $a\text{-MnO}_2 \cdot n\text{H}_2\text{O}$ was measured with N_2 gas to be 303 m²/g.

The electrode was formed by mixing 70 wt% $a\text{-MnO}_2 \cdot n\text{H}_2\text{O}$, 25 wt% acetylene black, and 5 wt% PTFE as binder before rolling into a thin sheet of uniform thickness. Pellets cut out of the sheet were cold-pressed at 4 ton/cm² for 10 s with a hand oil press onto a current collector that was made by welding titanium ex-met on tantalum foil.

The electrode performance was measured in a beaker-type electrochemical cell equipped with the working electrode, a platinum-gauze counter electrode, and a standard calomel reference electrode (SCE). The geometric surface area of the working electrode was 0.25 cm². The electrolyte was a 2M KCl aqueous solution with a pH adjusted to 6.7.

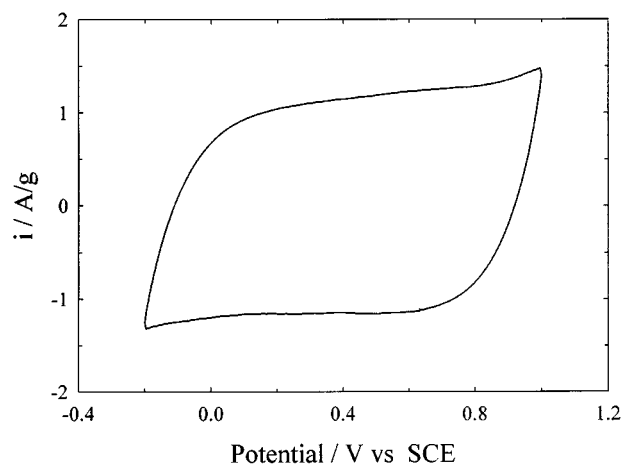


FIG. 1. Cyclic voltammogram taken at 5 mV/s between -0.2 and $+1.0$ V versus SCE for amorphous $\text{MnO}_2 \cdot n\text{H}_2\text{O}$ in 2 M KCl aqueous electrolyte.

Figure 1 shows the cyclic voltammogram (CV) for 2.55 mg of active $\alpha\text{-MnO}_2 \cdot n\text{H}_2\text{O}$ between -0.2 and $+1.0$ V versus SCE taken at a sweep rate of 5 mV/s. The curve shows no peaks, which indicates that the electrode capacitor is charged and discharged at a constant rate over the complete cycle. Moreover, the CV shows a mirror image with respect to the zero-current line and a rapid current response on voltage reversal at each end potential. These features indicate that the working K^+ ion has a rapid chemisorption/desorption reaction rate. The specific discharge and charge capacitances of this unoptimized material, as determined from the CV curves, were 198.3 and 199.1 F/g, respectively. This value is over one-fourth that of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ in 5.3 M H_2SO_4 at about 0.02 of the cost for an equivalent capacitance without the environmental disadvantage of a strong acid electrolyte. It is apparent that $\alpha\text{-MnO}_2 \cdot n\text{H}_2\text{O}$ in a mild 2 M KCl aqueous solution behaves as an ideal capacitor within the whole electrochemical stability window, -0.2 to $+1.0$ V vs SCE, of the electrolyte.

Figure 2 shows a linear variation of potential versus time for charge–discharge cycles swept at 2 mA/cm^2 . The measured specific discharge capacitance of 203 F/g remained unchanged for 100 cycles.

Figure 3 compares the short-circuit release of current for $\alpha\text{-MnO}_2 \cdot n\text{H}_2\text{O}$ in a 2 M KCl aqueous solution at pH 6.7 with $\alpha\text{-RuO}_2 \cdot n\text{H}_2\text{O}$ in 5.3 M H_2SO_4 for 4 mg each of active material after charging to $+1.0$ V. The $\alpha\text{-MnO}_2 \cdot n\text{H}_2\text{O}$ showed an initial current of 0.23 A/cm^2 and a total release of 3.8 C/cm^2 ; the $\alpha\text{-RuO}_2 \cdot n\text{H}_2\text{O}$ released 11.1 C/cm^2 with an initial current of 0.31 A/cm^2 . However, the rate of release of charge normalized to the total charge stored was faster for the $\alpha\text{-MnO}_2 \cdot n\text{H}_2\text{O}$ electrode, Fig. 3b. For example, the time to deliver 90% of the total charge stored in $\alpha\text{-MnO}_2 \cdot n\text{H}_2\text{O}$ took only 79% as long as that for

$\alpha\text{-RuO}_2 \cdot n\text{H}_2\text{O}$. Since the H^+ ion has a greater mobility in 5.3 M H_2SO_4 than the K^+ ion in 2 M KCl aqueous solution, this result indicates that the rate of discharge may not depend only on the mobility of the working ion, but also on the time for desorption from the surface. In either case, we would expect the performance with Na^+ and Li^+ ions to be slower as they require formation of a larger hydration sphere in the electrolyte.

To test this deduction, we compared the CVs for 2 M KCl, NaCl, and LiCl aqueous solutions taken at the same sweep rate of 5 mV/s between -0.2 and $+1.0$ V versus SCE, Fig. 4. Whereas the KCl solution gave almost ideal supercapacitor behavior, the CV for the NaCl solution shows that the current response on reversing the potential at the two end potentials is not fast enough to maintain a mirror-image shape. The CV for LiCl indicates an even slower response.

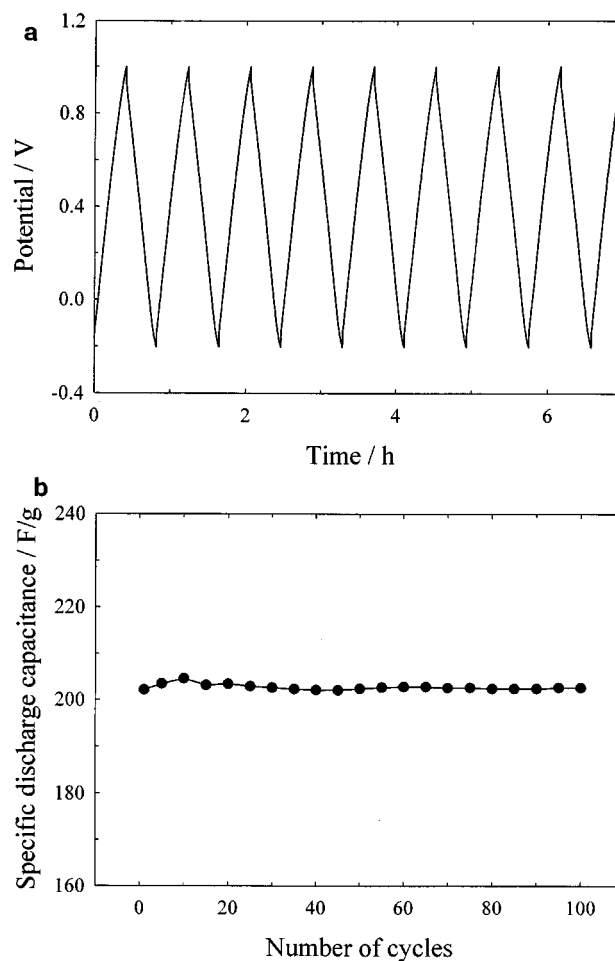


FIG. 2. (a) Electrode potential versus time and (b) specific discharge capacitance versus cycle number of 2.98 mg of amorphous $\text{MnO}_2 \cdot n\text{H}_2\text{O}$ in 2 M KCl aqueous electrolyte cycled between -0.2 and $+1.0$ V relative to SCE.

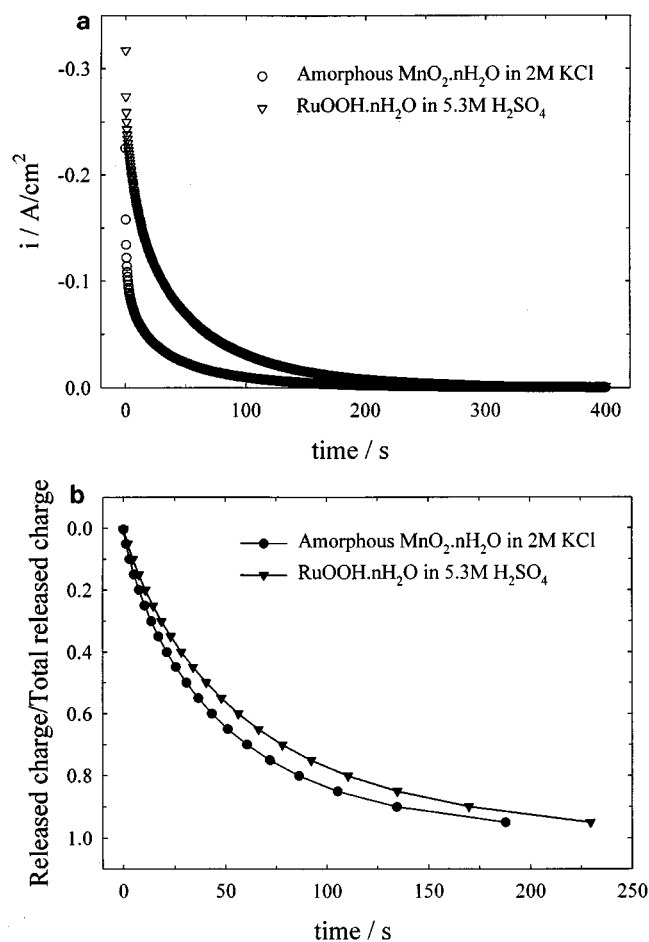


FIG. 3. (a) Discharge current versus time for amorphous $MnO_2 \cdot nH_2O$ in 2 M KCl aqueous electrolyte and $RuOOH \cdot nH_2O$ in 5.3 M H_2SO_4 aqueous electrolyte after charging to +1.0 V. (b) Comparison of time to release the normalized stored charge of amorphous $MnO_2 \cdot nH_2O$ in 2 M KCl aqueous electrolyte and $RuOOH \cdot nH_2O$ in 5.3 M H_2SO_4 aqueous solution.

Finally, the use of 2 M KCl with $a-RuO_2 \cdot nH_2O$ lowered the capacity to about 1/3 that with 5.3 M H_2SO_4 . We interpret this result to indicate that the K^+ ions chemisorb to three surface oxygen, whereas the protons chemisorb to one.

We conclude that mild KCl aqueous solution can replace a strong acid such as H_2SO_4 as the electrolyte of a supercapacitor and that its use can provide access to a wider range of electrode materials, e.g., $a-MnO_2 \cdot nH_2O$, with even some improvement in the rate of the charge, normalized to the total charge stored, is released on short-circuit discharge. However, the larger K^+ ion appears to bond to three surface oxygen, whereas the proton bonds to only one, which may lower the ideal capacity to be achieved to about 1/3 that obtained in $a-RuO_2 \cdot nH_2O$ in 5.3 M H_2SO_4 .

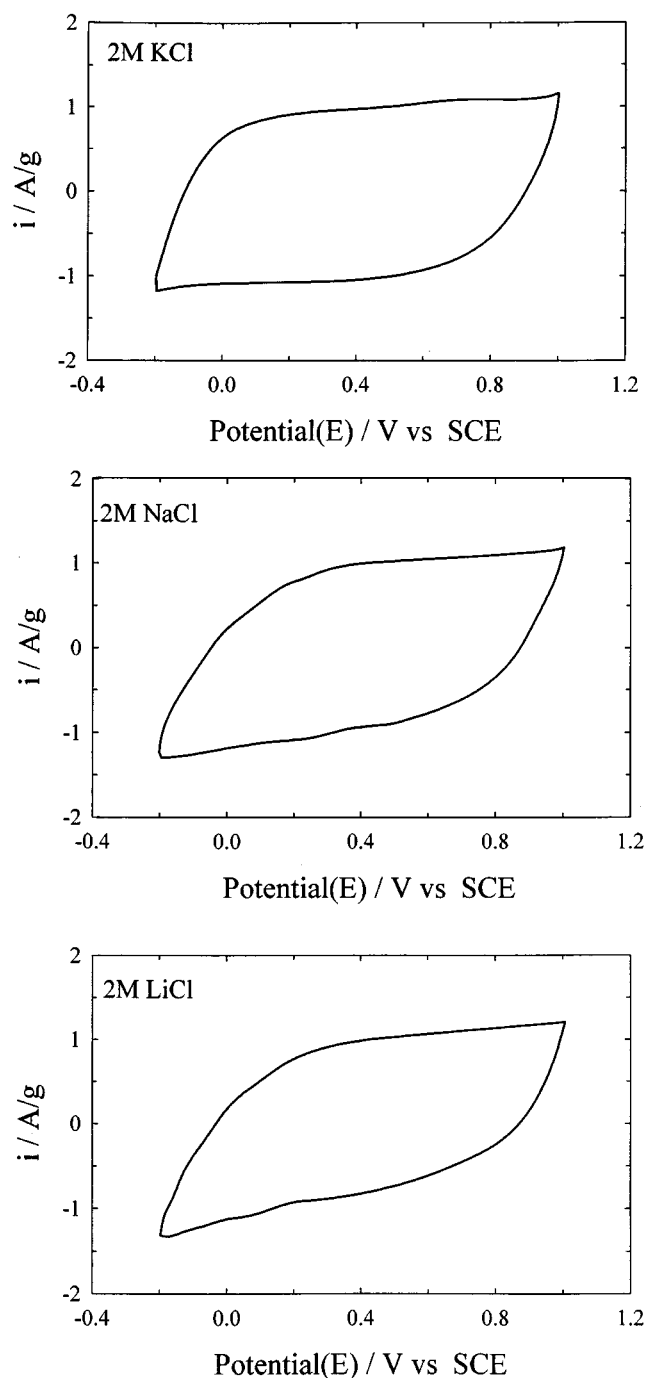


FIG. 4. Cyclic voltammograms at 5 mV/s of an amorphous $MnO_2 \cdot nH_2O$ electrode between -0.2 and +1.0 V versus SCE in 2 M ACl ($A = Li, Na, K$) electrolyte with Pt-gauze counter electrode.

ACKNOWLEDGMENTS

The authors thank the Robert A. Welch Foundation, Houston, TX, and the Institution for Advanced Technology, University of Texas, for financial support.

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