

Ideal Supercapacitor Behavior of Amorphous $V_2O_5 \cdot nH_2O$ in Potassium Chloride (KCl) Aqueous Solution

Hee Y. Lee and J. B. Goodenough

Texas Materials Institute, ETC 9.102, University of Texas at Austin, Austin, Texas 78712-1063

Received February 11, 1999; accepted May 10, 1999

Amorphous $a-V_2O_5 \cdot nH_2O$ in mild KCl aqueous electrolyte proves to be an excellent electrode for a faradaic electrochemical capacitor. Cyclic voltammograms versus SCE give ideal capacitor behavior between 0.0 and +0.8 V at pH 6.67 and between -0.2 and +0.8 V at pH 2.32 with, respectively, a constant specific capacitance over 100 cycles of ca. 350 and 290 F/g, respectively. On short-circuit, $a-V_2O_5 \cdot nH_2O$ in 2 M KCl aqueous solution at pH 2.32 gave an initial current density of 0.28 A/cm² and a total released charge of 4.5 C/cm², which is to be compared with 0.32 A/cm² and 11.1 C/cm² for RuOOH · nH_2O in 5.3 M H₂SO₄. Moreover, half the stored charge was released 1.6 times faster from the $a-V_2O_5 \cdot nH_2O$ electrode. These results demonstrate that the K⁺ ion can be used as the working ion in a faradaic capacitor, which frees the search for new materials from the constraint of working in a strong acid aqueous medium. © 1999 Academic Press

INTRODUCTION

The ability to deliver high power over limited time intervals would enhance the versatility of a portable electric power source that relies on a rechargeable battery. Therefore, electrochemical capacitors have been investigated intensively as auxiliary units in a hybrid battery-capacitor power supply (1). An electrochemical double-layer capacitor (EDLC) uses the physical separation between physisorbed ions in the electrolyte and a surface charge on a metallic electrode of large surface area (2); a faradaic capacitor (supercapacitor) uses the separation between a reduced cation at the surface of an amorphous metallic-oxide electrode and a cation chemisorbed to a shared oxide ion. Amorphous, hydrated RuO₂ has attracted particular attention as a supercapacitor since $a-RuOOH \cdot nH_2O$ can be reversibly oxidized to $a-RuO_2 \cdot nH_2O$ and reduced to $a-Ru(OH)_2 \cdot nH_2O$ over many cycles in a strong acid medium; this surface reaction corresponds to nearly one proton per Ru atom and yields a capacitance of over 700 F/g (3), which is significantly greater than has been achieved with an EDLC (4). Unfortunately $RuOOH \cdot nH_2O$ is too expensive to be

commercially attractive, which has stimulated a search for an alternative electrode material. The proton has the highest mobility in an aqueous electrolyte, and its small size allows it to chemisorb to a single oxide ion; therefore the electrolyte of choice has been a strong acid aqueous solution. However, a strong acid medium is environmentally harmful and the number of oxides having appropriate redox energies that are stable in a strong acid solution is extremely limited. Of these, the phosphopolymolybdate $H_3PMo_{12}O_{40} \cdot nH_2O$ appeared to be a promising candidate since it is stable in acid and all of the Mo(VI) atoms are at the surface of a Keggin polyanion $(PMo_{12}O_{40})^{3-}$, but this unit can only be reduced by one proton per surface Mo₃ cluster within the window of an aqueous electrolyte (5).

In order to avoid the problems associated with a strong-acid electrolyte, we decided to explore the use of a mild potassium-chloride (KCl) aqueous electrolyte in a faradaic supercapacitor since the K⁺ ion is known to have a relatively high mobility in aqueous medium. Although the K⁺ ion is too large to chemisorb at a single surface oxide ion, nevertheless we were able to show that unlike crystalline $K_xMnO_2 \cdot nH_2O$, amorphous $a-MnO_2 \cdot nH_2O$ in neutral KCl aqueous electrolyte behaves as an ideal capacitor with a relatively large capacitance of ca. 200 F/g (6, 7). In this paper, we report that amorphous $a-V_2O_5 \cdot nH_2O$ also shows ideal capacitor behavior in KCl aqueous electrolyte with a somewhat larger capacitance of ca. 350 F/g.

EXPERIMENTAL DETAILS

Amorphous vanadium oxide ($a-V_2O_5 \cdot nH_2O$) was prepared by quenching V₂O₅ fine powder heated at 950°C for 30 min into a bath of deionized water. The dark brown precipitate was filtered with a ceramic filter, washed several times with deionized water and ethanol, and then dried at room temperature.

The electrode for the electrochemical study was made by ball-milling for 25 min 70 wt.% $a-V_2O_5 \cdot nH_2O$, 25 wt.% acetylene black, and 5 wt.% PTFE as binder and then rolling the mix into a thin sheet of uniform thickness. Pellets

were cold-pressed onto a current collector that was made by welding titanium (Ti) ex-met on tantalum (Ta) foil at 4 ton/cm² for 10 s in a hand oil press.

A beaker-type electrochemical cell equipped with a working electrode, a platinum-gauze counter electrode, and a standard calomel reference electrode (SCE) was used for measuring the electrochemical properties of the working electrode and its performance as a faradaic supercapacitor. The geometric surface area of the working electrode was 0.25 cm². Adjustment of the pH of the KCl electrolyte was carried out by adding 1 M KHSO₄ solution. The electrochemical measurements included cyclic voltammetry (CV) and DC-current charge-discharge cycling in a 2 M KCl aqueous solution as electrolyte. The CV was recorded at a 5 mV/s sweep rate with an M273 galvanostat/potentiostat (EG&G PARC). The DC-current charge-discharge cycling was carried out galvanostatically with an automated battery-testing system (Arbin Co.).

Powder X-ray diffraction (XRD) was used to confirm the amorphous character of the a-V₂O₅·nH₂O.

RESULTS AND DISCUSSION

Figure 1a shows the XRD pattern of the as-prepared a-V₂O₅·nH₂O powder. The lack of any discernible diffraction peaks indicates that amorphous a-V₂O₅·nH₂O was successfully prepared. The need for an amorphous product was demonstrated for the case of a-MnO₂·nH₂O (7).

Figure 2 shows the CVs in 2 M KCl aqueous solution at pH 6.67 of an electrode of 1.62 mg active a-V₂O₅·nH₂O taken over various potential ranges versus SCE at a sweep rate of 5 mV/s. Figure 2a shows that on sweeping below -0.24 V vs SCE, the electrode appears to exhibit a huge

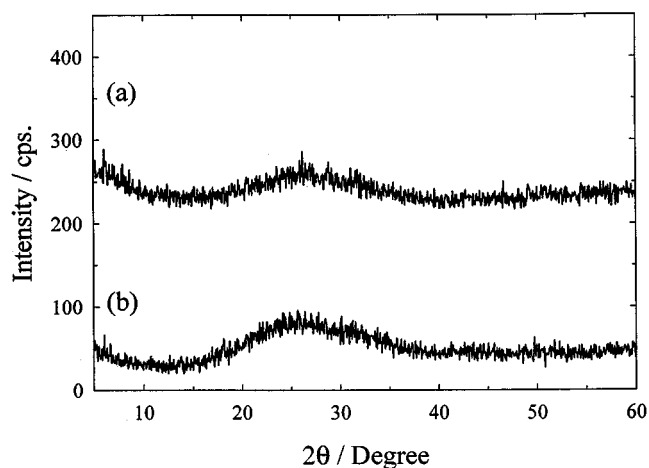


FIG. 1. X-ray diffraction patterns of (a) as-prepared a-V₂O₅·nH₂O powder and (b) a composite electrode consisting of a-V₂O₅·nH₂O, acetylene black, and Teflon after 100 cycles at 2 mA/cm² between -0.2 and +0.8 V in 2 M KCl electrolyte at pH 6.67.

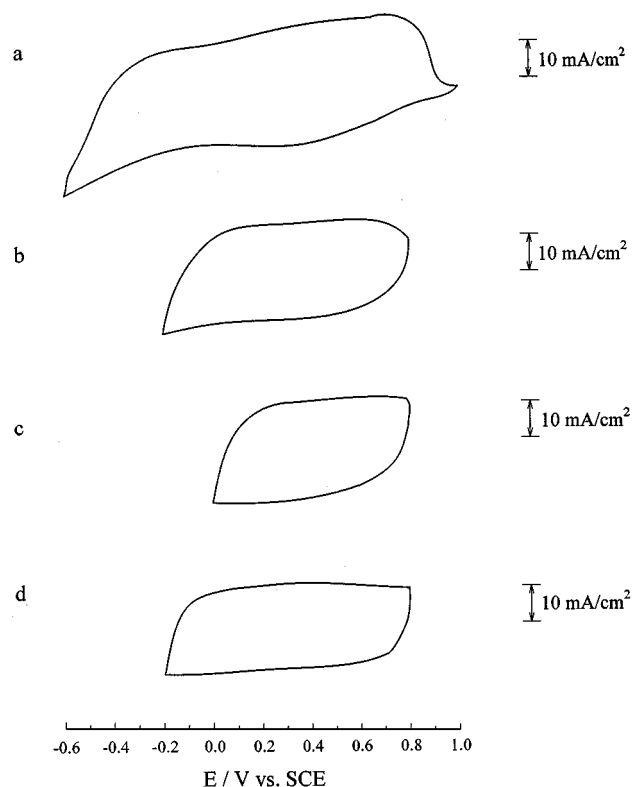


FIG. 2. Cyclic voltammogram taken at 5 mV/s in 2 M KCl aqueous electrolyte: (a) between -0.6 and +1.0 V at pH 6.67, (b) between -0.2 and +0.8 V at pH 6.67, (c) between 0.0 and +0.8 V at pH 6.67, and (d) between -0.2 and +0.8 V at pH 2.32.

overpotential against H₂ evolution. Even at applied voltages of -0.6 V, no H₂ evolution was observed. The CV curve of Fig. 2b is featureless, which shows that the chemisorption of the electrolyte K⁺ ions onto the a-V₂O₅·nH₂O occurs at a constant rate over the potential range -0.2 to +0.8 V vs SCE. However, some current tailing is observed at the end of the cathodic scan; the electrolyte took on a yellow coloring after 100 cycles and the electrode capacitance was reduced, but without any degradation of the shape of the CV. Reducing the scanning potential range to 0.0 to +0.8 V, Fig. 2c, eliminated the current tailing as well as the loss of capacitance and the yellowing of the electrolyte on repeated cycling; we therefore conclude that the current tailing is due to a dissolution of a-V₂O₅ at more cathodic potentials rather than to a kinetic irreversibility.

With pH 6.67, dissolution of a-V₂O₅ begins at -0.1 V; it extends to -0.6 V in Fig. 2a. The shape of the CV in Fig. 2c shows a mirror image against the zero-current line, and the rate of current change on reversal of the potential sweep shows the mobility of the working K⁺ ion is high enough to make the system reversible kinetically (8). Figure 2d shows the CV for the same electrode at an electrolyte pH 2.32. In this electrolyte, an ideal capacitor behavior without current

tailing is found between -0.2 and $+0.8$ V, but the specific capacitance is a little smaller than that of Fig. 2c. It appears that an acidic condition helps to stabilize $a-V_2O_5 \cdot nH_2O$ at a cathodic potential lower than -0.1 V vs SCE; but some protons apparently chemisorb on the surface oxygen to block the chemisorption of K^+ ions.

Figure 3 shows the variation of potential versus time for charge-discharge cycles in potential regions -0.2 to 0.8 V at pH 2.32 and 0.0 to $+0.8$ V at pH 6.67 relative to SCE at 2 mA/cm^2 for two $a-V_2O_5 \cdot nH_2O$ electrodes in a 2 M KCl aqueous solution. The weight of active material was 2.71 and 2.41 mg for Figs. 3a and 3b, respectively. The relationship between potential and time is quite linear. Figure 3c shows that the measured specific discharge capacitances of these two unoptimized electrodes remained at 286.3 F/g for Fig. 3a and 346.4 F/g for Fig. 3b. Even though the specific

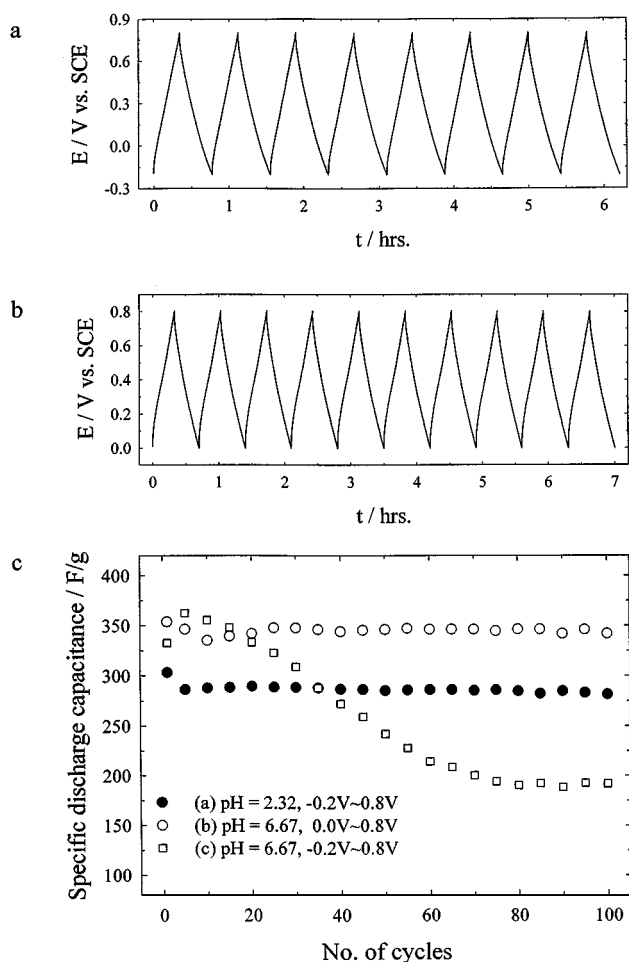


FIG. 3. Electrode potential versus time in 2 M KCl electrolyte (a) between -0.2 and $+0.8$ V at pH 2.32 and (b) between 0.0 and $+0.8$ V at pH 6.67. (c) Specific discharge capacitance versus cycle number in various experimental conditions: (○) between 0.0 and $+0.8$ V at pH 6.67, (●) between -0.2 and $+0.8$ V at pH 2.32, (□) between -0.2 and $+0.8$ V at pH 6.67.

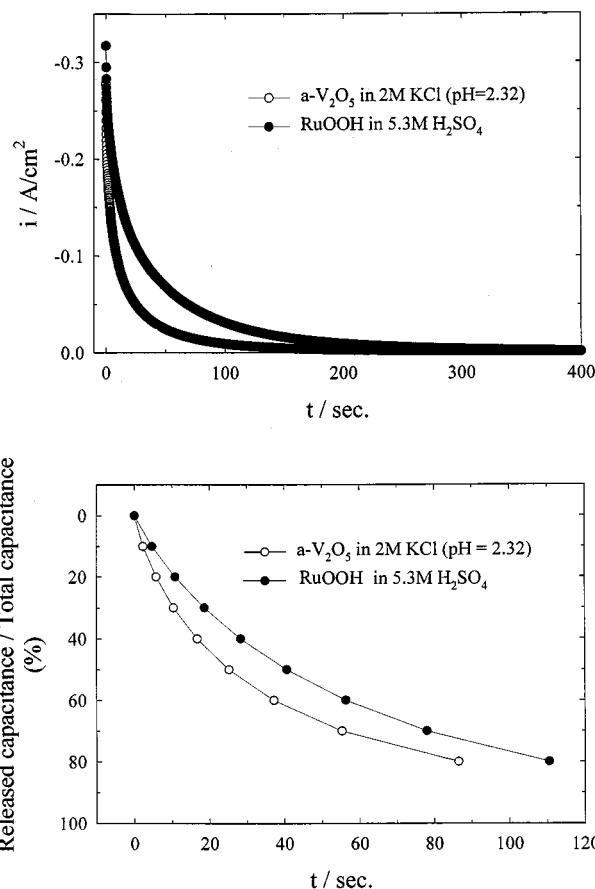


FIG. 4. (a) Discharge current versus time for $a-V_2O_5 \cdot nH_2O$ in 2 M KCl aqueous electrolyte at pH 2.32 and $a-RuOOH \cdot nH_2O$ in $5.3 \text{ M H}_2\text{SO}_4$ aqueous electrolyte after charging to $+0.8$ and $+1.0$ V, respectively. (b) Comparison of times to release the stored charge from $a-V_2O_5 \cdot nH_2O$ in 2 M KCl aqueous electrolyte at pH 2.32 and $a-RuOOH \cdot nH_2O$ in $5.3 \text{ M H}_2\text{SO}_4$ aqueous solution.

capacitance obtained between 0.0 and $+0.8$ V vs SCE at pH 6.67 is larger, the larger potential range at pH 2.32 gives a greater useful energy density. Increasing the potential range to -0.2 to $+0.8$ V at pH 6.67 caused the capacitance to fade; the electrolyte had a yellow coloring after 100 cycles. Although the shape of the CV remained similar, the current scale was reduced after 100 cycles. Figure 1b shows that the XRD pattern was also unchanged. These results give a clear indication that the capacitance fade was due to a loss of active material from the electrode to the electrolyte at the more cathodic potentials.

Figure 4a compares the short-circuit release of current for $a-V_2O_5 \cdot nH_2O$ in a 2 M KCl solution at pH 2.32 with that of an equal weight (4 mg) of active $RuOOH \cdot nH_2O$ in $5.3 \text{ M H}_2\text{SO}_4$ aqueous solution after charging to $+0.8$ and $+1.0$ V vs SCE, respectively. The $a-V_2O_5 \cdot nH_2O$ electrode gave an initial current of 0.28 A/cm^2 with a total charge release of 4.5 C/cm^2 ; the $a-RuOOH \cdot nH_2O$ electrode gave 0.32 A/cm^2 of initial current with a total charge release of

11.1 C/cm². However, the a-V₂O₅ · nH₂O electrode released its charge in a shorter time (Fig. 4b), taking only 62% as long to release half the total charge stored. This result indicates that the rate of discharge depends on the strength of chemisorption of the working ion as well as on its mobility; the H⁺ ion has the larger mobility in the electrolyte and the stronger bonding to the surface oxygen. The bond-breaking energy between oxygen and hydrogen is larger than that between oxygen and potassium in the gaseous phase.

CONCLUSIONS

In 2 M KCl aqueous solution, a-V₂O₅ · nH₂O is an electrode material that exhibits ideal capacitor behavior between 0.0 and +0.8 V at pH 6.67 and between -0.2 and +0.8 V at pH 2.32; the electrode had a constant discharge capacitance over 100 cycles of 286.3 F/g at pH 6.67 and 346.4 F/g at pH 2.32. The capacitance approaches half that of a-RuOOH · nH₂O in 5.3 M H₂SO₄ electrolyte and releases half its stored energy 1.6 times faster than does a-RuOOH · nH₂O. The faster discharge time reveals that the mobility of the working ion in the electrolyte is not the only determinant of speed of discharge; the binding energy of the chemisorbed ion to the surface also plays an important role. At a material cost only 1/6 that of RuO₂ and in the absence of the environmental costs associated with a strong-acid

electrolyte, supercapacitors based on a-V₂O₅ · nH₂O in a mild 2 M KCl solution offer a commercially attractive auxiliary to the secondary-battery system that must occasionally deliver short intervals of high power.

ACKNOWLEDGMENTS

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

REFERENCES

1. A. F. Bruke and T. C. Murphy, in "Materials for Electrochemical Energy Storage and Conversion—Batteries, Capacitors and Fuel Cells," MRS Symp. Proc. Vol. 393, p. 375, 1995.
2. M. Waidhas and K. Mund, in "Proceedings of the Symposium on Electrochemical Capacitor II" (F. M. Delnick, D. Ingersoll, X. Andrieu, and K. Naoi, Eds.), p. 180. The Electrochemical Society, Pennington, NJ, 1996.
3. J. P. Zheng, P. J. Cygan, and T. R. Jow, *J. Electrochem. Soc.* **142**, 2699 (1995).
4. I. D. Raistrick and R. J. Sherman, in "Materials and Processes for Energy Conversion and Storage" (S. Srinivasan, S. Wagner, and H. Wroblowa, Eds.), p. 582. The Electrochemical Society, Pennington, NJ, 1987.
5. A. Yamada and J. B. Goodenough, *J. Electrochem. Soc.* **145**, 737 (1998).
6. H. Y. Lee and J. B. Goodenough, *J. Solid State Chem.* **144**, 220 (1990).
7. H. Y. Lee, V. Manivannan, and J. B. Goodenough, unpublished.
8. B. E. Conway, *J. Electrochem. Soc.* **138**, 1539 (1991).