

Sodium insertion into vanadium pentoxide in methanesulfonyl chloride–aluminum chloride ionic liquid

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Abstract

Methanesulfonyl chloride (MSC) forms a room temperature ionic liquid with AlCl_3 . The electrochemical properties of vanadium pentoxide (V_2O_5) films prepared by the sol–gel route were studied in this electrolyte. As a potential cathode, sodium is reversibly intercalated into the V_2O_5 film up to a stoichiometry of 1.6 mole Na/mole V_2O_5 (–1 V versus $\text{Al(III)/Al} < 1.5$ V) after the first discharge. The diffusion coefficient (D_{Na^+}) in the V_2O_5 film was determined to be between $5\text{E}–14$ and $9\text{E}–12$ cm^2/s using the potentiostatic intermittent-titration technique. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Room temperature lithium batteries typically use a lithium metal or lithium–carbon anode in a room temperature ionic liquid as electrolyte [1,2]. Sodium anodes, however, are also of interest. The most frequently studied these molten salts are the chloroaluminate, such as $\text{AlCl}_3 + \text{BPC}$ (1-(1-butyl)pyridium chloride) and $\text{AlCl}_3 + \text{EMIC}$ (1-ethyl-3-methylimidazolium chloride) [3,4]. In particular, EMIC-containing electrolytes have drawn much attention for high energy density batteries as well as electrodeposition and chemical synthesis, due to their high ionic conductivity, low volatility and incombustibility [5–9].

The negative voltage limit of EMIC melts is +0.2 V versus Na/Na^+ , marginal for use in sodium metal batteries. Angell and colleagues [10] proposed new ionic liquids with methanesulfonyl chloride (MSC) replacing EMIC. The negative limit of these melts was 1 V beyond the sodium redox couple, indicating the potential anodic stability of these ambient-temperature electrolytes. Park et al. [11] investigated the sodium plating–stripping reaction in methanesulfonyl chloride molten salt electrolyte using an electrochemical quartz crystal microbalance (EQCM), finding reasonable coulombic efficiencies and current densities, thus pointing the way to an operational sodium anode.

As a cathode in such a battery, electrochemical insertion of ions into vanadium pentoxide (V_2O_5) has definite potential, as it has in room temperature lithium batteries [12–14] and electrochromic devices [15]. Thin films of V_2O_5 have been prepared by various methods such as vacuum evaporation, sputtering, chemical vapor depositions; however, sol–gel methods provide even easier processing of large scale films. Our present work therefore is to study sodium ion insertion into V_2O_5 thin films prepared by a sol–gel technique based on a vanadium alkoxide precursor in a methanesulfonyl chloride–aluminum chloride electrolyte to assess potential application in a sodium battery.

2. Experiment

2.1. Preparation of V_2O_5 films

As described by Meulenkamp et al. [14], the organic precursor used in this work was vanadium isopropoxide $\text{VO}(\text{OC}_3\text{H}_7)_3$ (Aldrich) dissolved in isopropanol (Aldrich). The alkoxide/solvent ratio was 2.5 wt.%, which allowed us to obtain a clear, stable solution suitable for making films. V_2O_5 films were formed by a dip-coating process on Ni substrate (99.7% pure, Johnson–Matthey Catalog Company) that were lowered into the solution, and then withdrawn at a uniform rate. In order to obtain thicker films the dipping process was repeated many times, with intermediate heating in an oven at 180°C for 5 min to prevent dissolution of prior

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layers by the solution. The films were then heated at different temperatures for 4 h in the oven to remove residual solvent and organic components.

2.2. Electrochemistry

All experiments were carried out in a nitrogen-filled glove box (Vacuum Atmospheres Company) with a combined concentration of oxygen and water below 10 ppm. The MSC room temperature ionic liquid was used as the electrolyte; it was prepared by mixing 65 mole MSC (>99.5% pure, Aldrich) with 35 mol% aluminum chloride (Aldrich), and then adding 2.5 M sodium chloride (99.999% pure, Aldrich) [11]. The electrochemical tests were done using a traditional three-electrode electrochemical cell. The above-mentioned V_2O_5 film on a Ni substrate was used as working electrode; the counter electrode is a large surface area Pt foil. The reference electrode was formed by immersing a 0.5 mm diameter aluminum wire into an acidic EMIC (0.4 mole fraction) and aluminum chloride (0.6 mole fraction) ionic liquid in a borosilicate glass tube with a fine glass frit [6,7]. This acidic melt permits the reversible aluminum redox reaction to maintain a stable reference potential. A Princeton Applied Research 273 potentiostat/galvanostat interfaced with a personal computer using model a 270/250 research electrochemistry software were used for routine electrochemical measurements. The electrochemical experiments were performed at room temperature.

3. Results and discussion

The electrochemical properties of films heat-treated to 200, 250, 300, 350, and 400°C were tested at 200°C. Little sodium insertion was detected, as evidenced by very small currents; the film apparently still contains organic residue, denying effective Na^+ intercalation. The film prepared at 250°C is known to be solvent-free and amorphous [16], while at 300°C it is composed of an amorphous phase and a crystalline one [17]. At 350 and 400°C the films are yellow-orange, typical of crystalline V_2O_5 . The electrochemical properties of the amorphous (the 250°C film) and crystalline (the 400°C film) V_2O_5 films were investigated hereafter.

Cyclic voltammetry (CV) was used to investigate sodium intercalation into the V_2O_5 film in the MSC ionic liquid. A typical CV measured at a sweep rate of 20 mV/s is shown in Fig. 1. In Fig. 1a, the V_2O_5 films were heat-treated to 250°C. Here a small background current was observed when the potential scan was run in the positive direction from the open-circuit voltage to 1.9 V. The cathodic current for sodium insertion into V_2O_5 film is seen to increase steadily when the potential was scanned from 1.9 to 0 V. On the reverse, positive scan the anodic current for sodium extraction out of V_2O_5 film was also seen to increase steadily. In the second sweep cycle, the current decreased; however, in subsequent cycles, the magnitude of the current changed

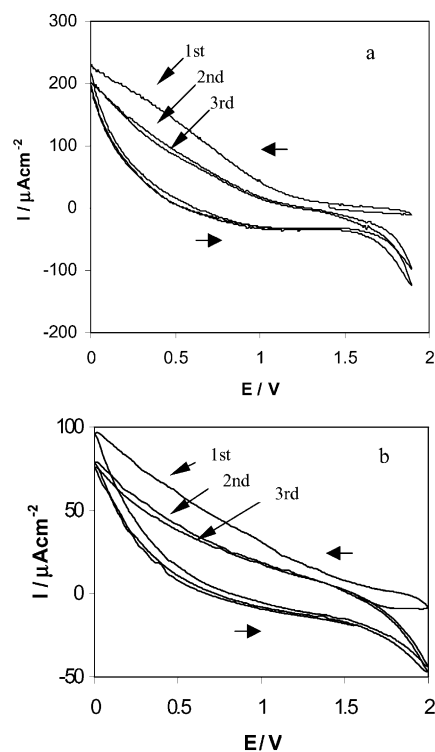


Fig. 1. Cyclic voltammogram for V_2O_5 films on Ni heat-treated to 250°C (a) and 400°C (b) in MSC ionic liquid. Scan rate: 20 mV/s.

only slightly. The CV results for V_2O_5 films Fig. 1b heat-treated to 400°C show similar behavior.

A critical parameter of any secondary battery is its coulombic efficiency in charge–discharge cycling. The coulombic efficiency is defined as 100 times the ratio of the number of coulombs passed during extraction of sodium (charging cycle) to the number passed during insertion of sodium (discharge cycle). If the coulombic efficiency is 100%, sodium can be intercalated reversibly into the V_2O_5 film, which would be necessary for a cathode in a sodium battery. From Fig. 1a in the first sweep cycle, the coulombic efficiency, ratio of the anodic (charging) and cathodic (discharging) charge was 27.3%. In the second sweep cycle, the corresponding coulombic efficiency is 44.5%. A similar coulombic efficiency is also seen in Fig. 1b. However, when the CV was performed in the potential range from 0.2 to 2 V at 20 mV/s (not shown), the corresponding efficiency is 97%.

Fig. 2 shows a typical chronoamperogram of V_2O_5 film in MSC molten salt, where the V_2O_5 films were heat-treated to 250 °C. Before the experiment, the potential was held at 1.7 V for 10 min to remove any sodium from the V_2O_5 film. The potential was held at 0.5 V for 5 s for insertion of sodium into the V_2O_5 film, and then stepped to 1.7 V for 30 s for extraction of sodium out of the V_2O_5 film. The coulombic efficiency was found to be 98%, indicating sodium can be intercalated with coulombic reversibility into V_2O_5 film. The chronoamperogram results of V_2O_5 films

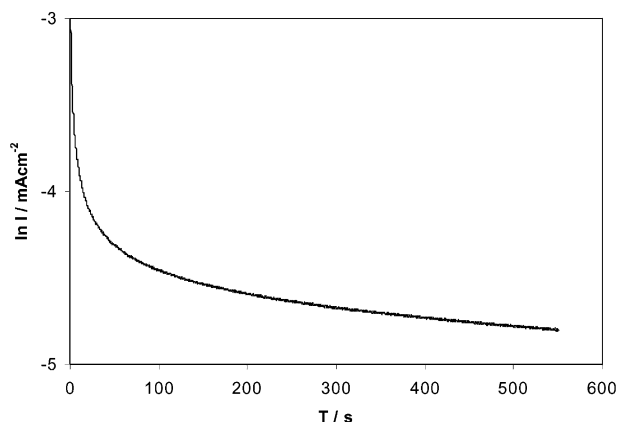


Fig. 2. Chronoamperogram on V_2O_5 film on Ni heat-treated to 250°C in MSC ionic liquid. Insertion and extraction were at 0.5 V for 5 s and 1.7 V for 50 s .

prepared at 400°C exhibit this same sodium intercalation reversibility, although at a lower current density.

These results correspond to the insertion/de-insertion of sodium ions according to the following reaction.



The fact that in the third and further cycles, the magnitude of the current changed only slightly, indicates that sodium intercalation into V_2O_5 film is initially accompanied by a non-reversible lattice deformation, possibly a relaxation of the oxygen around reduced vanadium, as seen in $\text{Na}_xV_2O_5$. The lattice is evidently transformed into a new structure and does not revert to the original structure as sodium is subsequently extracted. The initial loss of charge is followed by a stable and reproducible response for the $\text{Na}_xV_2O_5$. These results show that the rate of de-insertion of sodium is slower than that of insertion of sodium. It is interesting to note that West et al. [18] found similar phenomena in constant current discharge experiments using V_2O_5 as the cathode material in a solid-state sodium battery.

In order to establish the stoichiometry of the insertion reaction, the experimental equivalent weight of the inserted species was calculated from the constant current discharge measurement, assuming one electron transfer per equivalent of sodium. Fig. 3 shows the discharge curves for the V_2O_5

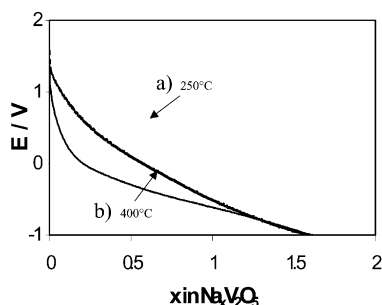


Fig. 3. Potential vs. Na composition ($E-x$) curves ($50\ \mu\text{A}/\text{cm}^2$) in V_2O_5 films on Ni heat-treated to 250°C (curve a) and 400°C (curve b) in MSC ionic liquid.

films at a constant current of $50\ \mu\text{A}/\text{cm}^2$ in MSC molten salt. In Fig. 3, the V_2O_5 films were heat-treated to 250°C (a) and 400°C (b), respectively. There are no inflection points in the $E-x$ curve, implying a quite homogeneous Na^+ intercalation process. This behavior is not in agreement with the data available in the literature: there are inflection points in the $E-x$ curve with V_2O_5 prepared by thermal decomposition of ammonium metavanadate in oxygen as cathode materials in solid-state sodium batteries [18]. The latter is also seen in the lithium insertion work into vanadia-xerogel films of Shouji using an EQCM [19].

The chemical diffusion coefficient (D_{Na^+}) is an important parameter for the intercalation process; the diffusion coefficients were measured using the potentiostatic intermittent-titration technique [20]. In this method, the current generated due to an applied voltage step (V_1-V_2) is measured as a function of time. The measured current decayed as the sodium ions diffused through the film. The step was terminated when the current reached a specified minimum, e.g. 1% of the maximum current at the onset of the applied potential. A new step began by applying another voltage step; these voltage steps can be to higher or lower potentials, allowing measurement of sodium into or out of the film.

The diffusion of sodium into a single-phase film in response to a voltage step can be modeled as one-dimensional transport based on Fick's second law,

$$\frac{\partial C_{\text{Na}}}{\partial t} = D \frac{\partial^2 C_{\text{Na}}}{\partial x^2}$$

where x is the distance into the film from the molten salt electrolyte interface; C_{Na} is the sodium concentration at x and time t , and D is the chemical diffusion coefficient. The initial and boundary conditions for diffusion into a finite thickness L , with a constant surface concentration, C_s , are

$$C_{\text{Na}} = C_0, \quad 0 \leq x \leq L, \quad t = 0$$

$$C_{\text{Na}} = C_s, \quad x = 0, \quad t > 0$$

$$\frac{\partial C_{\text{Na}}}{\partial x} = 0, \quad x = L, \quad t \geq 0$$

in this model, D is assumed to be constant over the small concentration range C_s-C_0 induced by the voltage step. It is also assumed that sodium enters the planar electrode only at the molten salt interface ($x = 0$), that the substrate (vanadia backing) is impenetrable, and that the material is single phase. Our dense film satisfies these geometrical requirements and the nickel is electrochemically inert at the cathode voltage.

A solution to this diffusion problem [21] is

$$C_{\text{Na}}(x, t) = C_s - (C_s - C_0) \frac{4}{\pi} \sum_{n=0}^{\infty} \left[\frac{1}{2n+1} \sin\left(\frac{(2n+1)\pi x}{2L}\right) \times \exp\left(-\frac{(2n+1)^2 \pi^2 D t}{4L^2}\right) \right]$$

The electric current is determined by the concentration gradient at the solid–electrolyte interface. In particular

$$I(t) = -zFS D \left(\frac{\partial C}{\partial x} \right)_{x=0},$$

$$I(t) = \frac{2zFS(C_s - C_0)D}{L} \sum_{n=0}^{\infty} \left[-\frac{(2n+1)^2 \pi^2 Dt}{4L^2} \right]$$

where z is the charge number of the electroactive species (equal to 1 for Na), F is Faraday’s constant, and S is the area of the cathode exposed to electrolyte. Even a long time ($Dt/4L^2 > 0.075$), a reasonably good approximation can be made by taking only the first term in the series as in

$$I(t) = I_0 \exp\left(-\frac{\pi^2 Dt}{4L^2}\right), \quad I_0 = \frac{2zFS(C_s - C_0)D}{L}$$

The chemical diffusion coefficient, D , can be obtained from the slope of the linear region in the plot of $\ln I(t)$ versus time, where

$$D = -\frac{d[\ln I]}{dt} \frac{4L^2}{\pi^2}$$

in the linear region of the plot. The voltage step applied was from the open circuit voltage of each film to lower voltage. Typical data are shown as Fig. 4. The logarithm of the

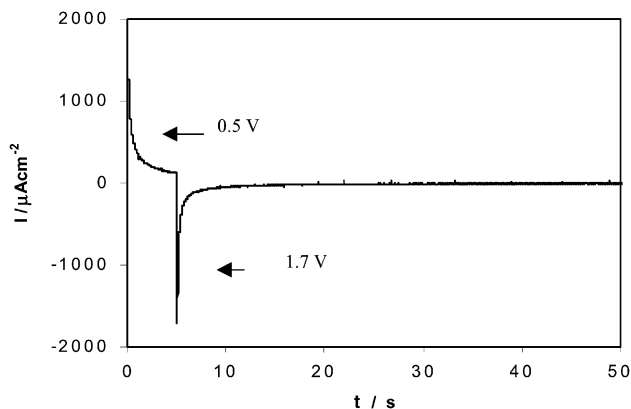


Fig. 4. Short time $\ln I(t)$ plot for a voltage step of 0.5 and 1.7 V for a V_2O_5 film in MSC ionic liquid.

current is plotted as a function of time for a single voltage step; it is seen to decrease sharply with time at the initial stage, and then decrease steadily with time. The slope $d[\ln I]/dt$ is determined from the straight line at the latter stage. The amount of sodium intercalated, x , was determined by integrating the measured current in the individual step.

The thickness of the V_2O_5 film was calculated from its mass and area. The chemical diffusion coefficient (D_{Na^+}) is plotted as a function of Na concentration for the V_2O_5 films in Fig. 5. In Fig. 5a and b, data are shown for the V_2O_5

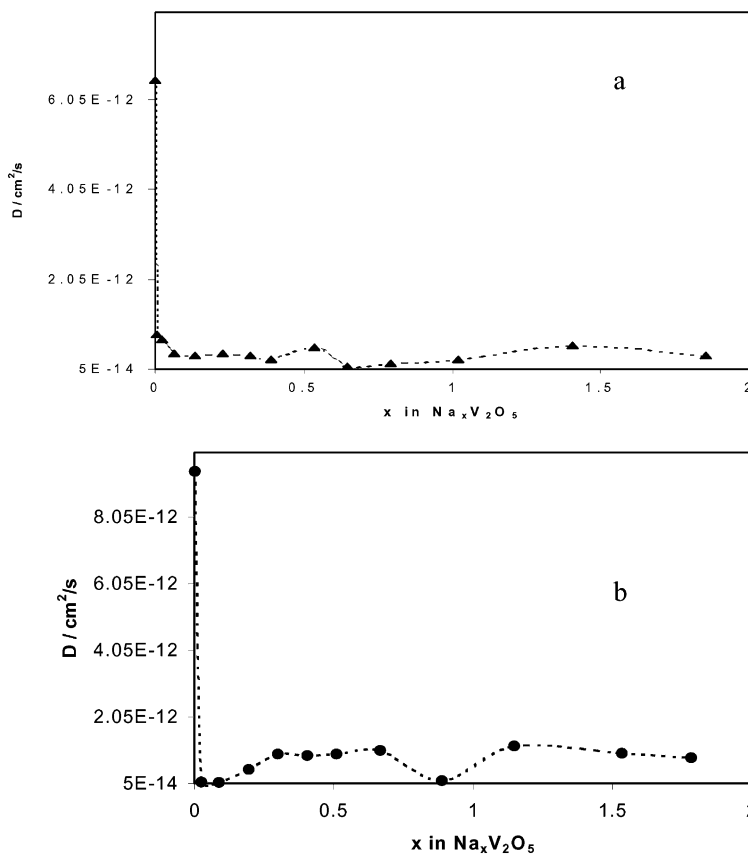


Fig. 5. Chemical diffusion coefficient (D_{Na^+}) vs. concentration (D_{Na^+-x}) in the V_2O_5 films on Ni heat-treated to 250°C (a) and 400°C (b) in MSC ionic liquid.

films had been heat-treated to 250 and 400°C, respectively. For very low values of x , D_{Na^+} is at first relatively high: D_{Na^+} for the V_2O_5 films prepared at 250 and 400°C is equal to $7\text{E}-12$ and $9\text{E}-12$ cm^2/s , respectively. But, as x increases, the diffusion coefficient decreases dramatically, reaching about $5\text{E}-13$ cm^2/s . In fact, ion diffusion seems to be facilitated by the insertion of a small amount of sodium. This phenomenon is explained by a structural rearrangement (parameter dilatation) provoked by the insertion of the first sodium ions. Surca et al. [17] observed a similar change between D_{Li^+} and x in V_2O_5 film as a cathode material for lithium ion battery. In crystalline V_2O_5 film, the values of D_{Li^+} are higher. They vary between 10^{-7} and 10^{-9} cm^2/s depending on the lithium ratio in the structure or on the structure phase [22–24]. The magnitude of D_{Na^+} is smaller than that of D_{Li^+} , but both may be limited by solvent carried with the ions [19].

The chemical diffusion coefficient (D_{Na^+}) of the V_2O_5 films is dependent of the depth of discharge state (i.e. intercalation concentration of sodium ion in the electrode, or x). The diffusion coefficient measured in the crystalline phase is generally of the same order of magnitude as that of the amorphous film, and fluctuates with the sodium composition with a broad range.

4. Conclusions

Thin films of V_2O_5 were prepared by a sol–gel technique and the Na chemical diffusion coefficient was measured using the potentiostatic intermittent-titration technique. The diffusion coefficient (D_{Na^+}) in the V_2O_5 film ranges from a minimum of $5\text{E}-14$ cm^2/s to a maximum of $9\text{E}-12$ cm^2/s . V_2O_5 films were found to have an insertion capacity of about 1.6 mole of sodium per mole of V_2O_5 . Upon sodium insertion V_2O_5 undergoes a phase change resulting in a new structure with stable and reproducible cycling properties. Sodium insertion into V_2O_5 in MSC molten salt shows high coulombic efficiency, up to 98%. With further development, V_2O_5 may be suitable as a cathode material in sodium batteries.

Acknowledgements

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