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Journal of Power Sources 97–98 (2001) 486–490

JOURNAL OF
POWER
SOURCES

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Study of lithium insertion into electrochemically synthesized sodium–vanadium oxide

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Received 23 June 2000; received in revised form 17 November 2000; accepted 4 December 2000

Abstract

We report herein on the electroanalytical behavior of $\text{Li}_x\text{Na}_y\text{V}_2\text{O}_5$ electrodes that were synthesized electrochemically from aqueous solutions of vanadyl and sodium sulphates, followed by thermal annealing (300°C).

The electrodes were comprised of monolithic layers deposited on a stainless steel plate. A capacity above 200 mAh/g could be obtained at relatively high rates (>C/3 h) and prolonged cycling (hundreds of charge–discharge cycles). As evident from FTIR and XPS measurements, the electrodes develop surface films due to interactions with CO_2 in the air and solution species. Electroanalytical data obtained from slow scan rate cyclic voltammetry (SSCV), potentiostatic intermittent titration (PITT), and impedance spectroscopy (EIS) are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Rechargeable Li batteries; Sodium–vanadium oxides; Electrochemical behavior; Impedance spectroscopy; Li-ion diffusion coefficient; Electrode surface chemistry

1. Introduction

Among the many transition metal oxides used as cathodes in rechargeable lithium batteries, vanadium pentoxide and sodium–vanadium oxides have attracted much attention [1] due to their promising discharge characteristics (e.g. high capacity and reversibility). It was shown in recent publications ([2,3] and references therein) that electrochemical synthesis of both V_2O_5 and $\text{Na}_y\text{V}_2\text{O}_5$ has advantages over other methods, for obtaining thin and homogeneous electrodes with a well-defined and controllable composition. It was possible to obtain by electrochemical deposition compact and monolithic thin films of vanadium oxide and vanadium bronze on metal substrates, that could be used as cathodes without the need of electroconductive additives and binder. The high capacity (>200 mAh/g) and the moderate redox potentials (around 3 V versus Li/Li^+) make $\text{Na}_y\text{V}_2\text{O}_5$ a suitable cathode for rechargeable batteries with lithium metal anodes. Their moderate voltage is advantageous because it enables the use of ethereal solutions or solid

electrolyte systems, based on polyethylene oxide derivatives in which lithium metal anodes are highly reversible.

In this paper, we concentrate on the electroanalytical characterization of electrochemically synthesized sodium–vanadium oxide $\text{Na}_y\text{V}_2\text{O}_5$ cathodes for Li and Li-ion batteries. The main emphasis in the present work relates to the cycling performance of the $\text{Na}_y\text{V}_2\text{O}_5$ cathodes and the Li insertion kinetic and transport properties. We also explored possible interactions between the cathodes and the electrolyte solutions, which probably affect the electrode's kinetics.

2. Experimental

Sodium–vanadium oxides were electrochemically synthesized from an aqueous electrolyte solution comprising vanadyl sulphate (0.2 M/l) and sodium sulphate (5 g/l of Na^+). The optimal conditions of the synthesis were as follows: current density of 7.5–12.5 mA/cm², pH of 1.8 and a temperature of 80–85°C [2]. Stainless steel plates or grids were used as substrates for sodium–vanadium oxide precipitates. The electrodes thus obtained were thermally annealed at 100–500°C for about 2–7 h. The active mass of the electrodes was 0.8–1.9 mg/cm². The sodium–vanadium

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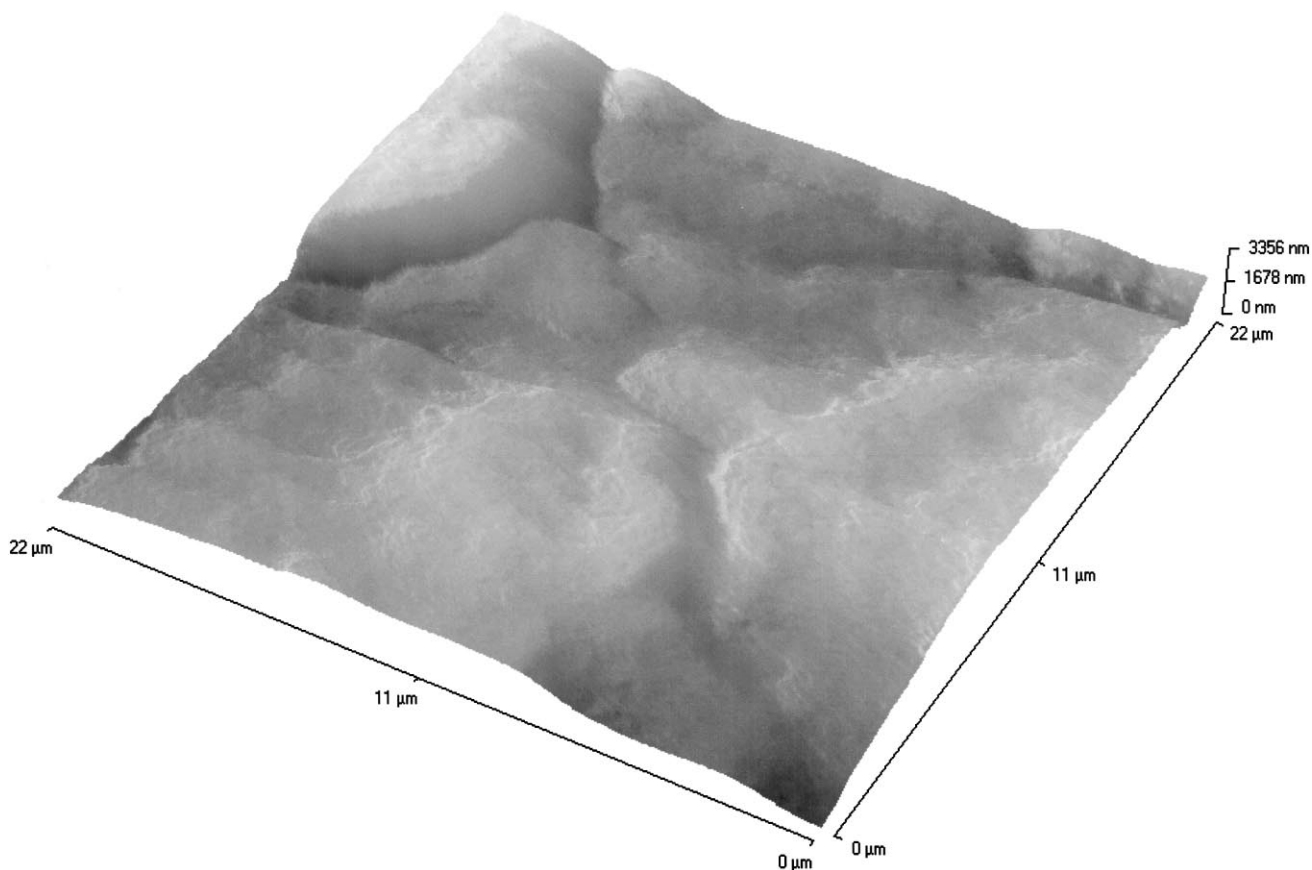


Fig. 1. A typical STM image of the sodium–vanadium oxide electrode obtained electrochemically from an aqueous electrolyte solution comprising vanadyl sulphate (0.2 M/l) and sodium sulphate (5 g/l of Na^+).

oxide layer was 2–4 μm thick, as estimated by SEM and STM techniques [4], and consisted of smooth multi-layered deposits with a characteristic roughness factor around 1.03–1.08 (Fig. 1). For the electrochemical measurements we used three-electrode rectangular cells filled with an electrolyte solution of ethylene carbonate (EC), dimethyl carbonate (DMC) (1:3 by volume, solvents from Merck, Li battery grade) and 1 M LiAsF_6 (FMC). The water content in the electrolyte was usually around 20 ppm. The electrochemical experiments, including impedance spectroscopy and potentiostatic intermittent titration, were performed as described previously [5–9]. For FTIR spectroscopic measurements in diffuse reflectance mode, we used the Magna 860 spectrometer (Nicolet) equipped with a DRIFT accessory (Harrick) placed in a homemade glove box under CO_2 - and H_2O -free atmosphere. XPS studies were performed using an AXIS-HS system from Kratos Analytical Inc., England.

3. Results and discussion

According to the XRD studies, the cathode material, obtained electrochemically from the aqueous VOSO_4 solution containing 5 g/l Na^+ , is a mixture of 25% V_2O_5 and 75% $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ bronze.

In Fig. 2a we present cyclic voltammograms obtained during repeated charge–discharge cycling with a thin electrode of sodium–vanadium oxide. The CVs can be characterized by a pair of pronounced cathodic and anodic peaks at 2.51 and 2.73 V, respectively. A shoulder appearing at 2.84 V in the cathodic sweep corresponds to that in the anodic sweep at 2.95 V.

We note that the positions of the two Li intercalation peaks at 2.8 and 2.5 V observed by Bach et al. [10] for $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ bronze cathodes prepared by a sol–gel method are very close to the position of the major cathodic peaks presented herein (related to our cyclic voltammetry data from the electrochemically synthesized cathodes). The cyclic voltammetric results obtained in the present work are somewhat different compared with those that we obtained previously with $\text{Na}_{0.33}\text{V}_2\text{O}_5$ cathodes synthesized electrochemically from a VOSO_4 solution containing 20 g/l Na^+ [2]. The main difference is that the first reduction peak in the CV of the $\text{Na}_{0.33}\text{V}_2\text{O}_5$ cathode is shifted 300 mV to lower potentials. In general, we found that in standard electrolyte solutions such as EC–DMC/ LiAsF_6 , a steady state behavior of these electrodes is achieved within the first three to five cycles. Forty subsequent galvanostatic cycles of the electrode related to Fig. 2 at C/10 and C/5 resulted only in a minor shifting of the second anodic peak to a more positive

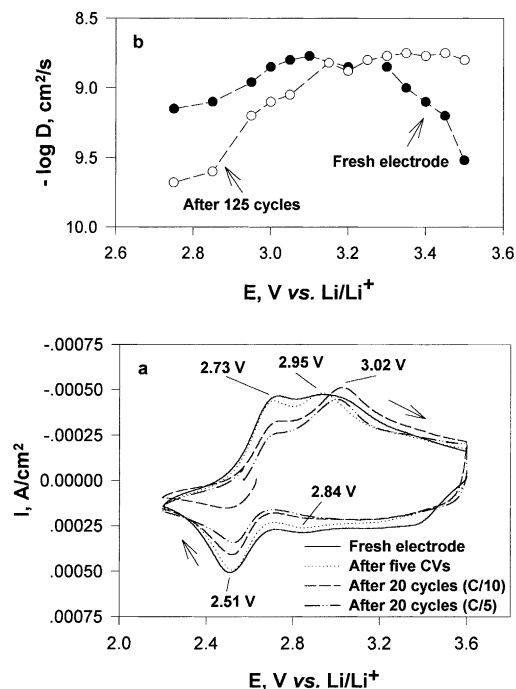


Fig. 2. (a) A comparison of the potentiodynamic responses of fresh and cycled sodium–vanadium oxide electrodes. Potential scan rate was 0.5 mV/s. EC:DMC (1:3)/LiAsF₆ 1 M solution. (The electrodes were thermally annealed at 300°C for 2.5 h after their electrochemical synthesis). (b) The potential-dependence of the Li chemical diffusion coefficient (D) measured with fresh and cycled electrodes (125 galvanostatic charge–discharge cycles) calculated from EIS (see text). Same electrodes as those related to (a).

potential. In addition, a shoulder in the anodic sweep appearing with the pristine electrodes develops into separate peaks positioned at 2.95 and 3.02 V upon prolonged cycling. This can be attributed to some kinetic changes at the electrode/electrolyte interface during lithium deintercalation from the aged electrode. Prolonged cycling of these electrodes results in only minor changes in their electro-analytical response: we see some evidence for more sluggish kinetics as prolonged cycling proceeds.

It is clearly demonstrated that in the 3.6–2.2 V potential range, the electrode is stable in repeated charge–discharge cycling and it provides a capacity ca. 215 mAh/g at C/20. Faster constant current cycling (C/2.5) decreases the discharge capacity to only 200 mAh/g. It should be noted that during prolonged galvanostatic cycling (at least 200 charge–discharge cycles) the average capacity of this electrode remains almost 200 mAh/g. The stability of these electrodes upon cycling is also demonstrated by displaying D , the chemical diffusion coefficient (calculated from impedance spectroscopy (EIS), see below), as a function of potential, for fresh and cycled electrodes. As demonstrated in Fig. 2b, D versus E calculated for a cycled electrode is, on the average, at the same order of magnitude as D versus E calculated for a fresh electrode.

When analyzing experimental sets of EIS measurements with fresh Na_xV₂O₅ electrodes (which underwent only

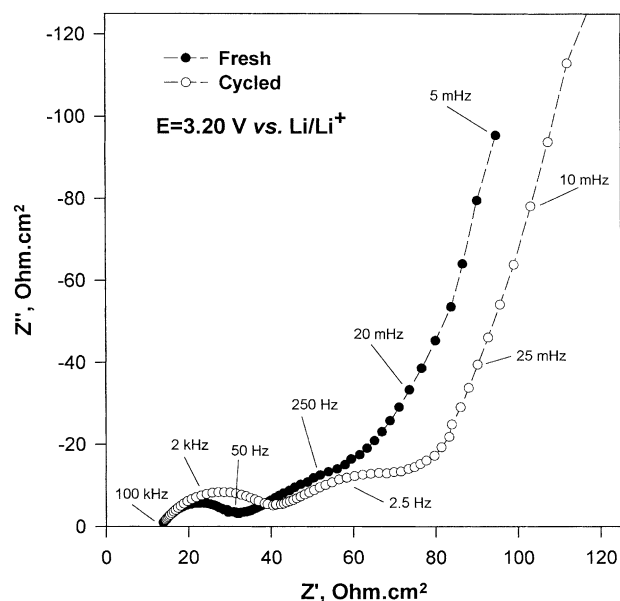


Fig. 3. Nyquist plots obtained at 3.20 V (vs. Li/Li⁺) from fresh and cycled sodium–vanadium oxide electrodes (indicated). EC:DMC (1:3)/LiAsF₆ 1 M solution.

several potentiodynamic CV cycles at different scan rates before the EIS measurements) and with the same electrodes after prolonged galvanostatic cycling, the same common features of the impedance spectra are found (Fig. 3). A depressed semicircle in the high-to-medium frequency range and another semicircle or an arc in the medium-to-low frequency range are observed in these spectra. These impedance features relate to two sets of time-constants. We attribute the high-to-medium semicircle to the impedance of surface films, which are formed on the electrode's surface due to reactions with solution species and the medium frequency semicircle, to the interfacial charge-transfer resistance related to slow Li⁺ transport at the surface film/active mass interface, coupled with a double-layer interfacial capacitance. It was found that the surface film resistance depends only slightly on the intercalation potential for both the fresh (pristine) and cycled cathodes. In contrast, the charge-transfer resistance is potential-dependent and increases considerably in the potential range of 2.8–2.3 V. We assumed that the pristine Na_xV₂O₅ cathode may contain a surface layer comprised of NaHCO₃ or Na₂CO₃ due to the reaction of the active mass with CO₂ in the air. This was proved by XPS studies, which clearly demonstrated the presence of the above carbonates on the surface (a characteristic carbon 1s peak at a binding energy around 290 eV). Fig. 4, which shows FTIR spectra of cathodes, provides some additional information on the surface chemistry of pristine and cycled sodium–vanadium oxide cathodes (EC:DMC (1:3)/LiAsF₆ solution). It shows IR peaks at 745 and 1006 cm⁻¹ in the spectrum of the pristine electrode that can be assigned to vibrations of V₂O₅. The IR peaks around 1610, 1400, and 850 cm⁻¹ may belong to surface

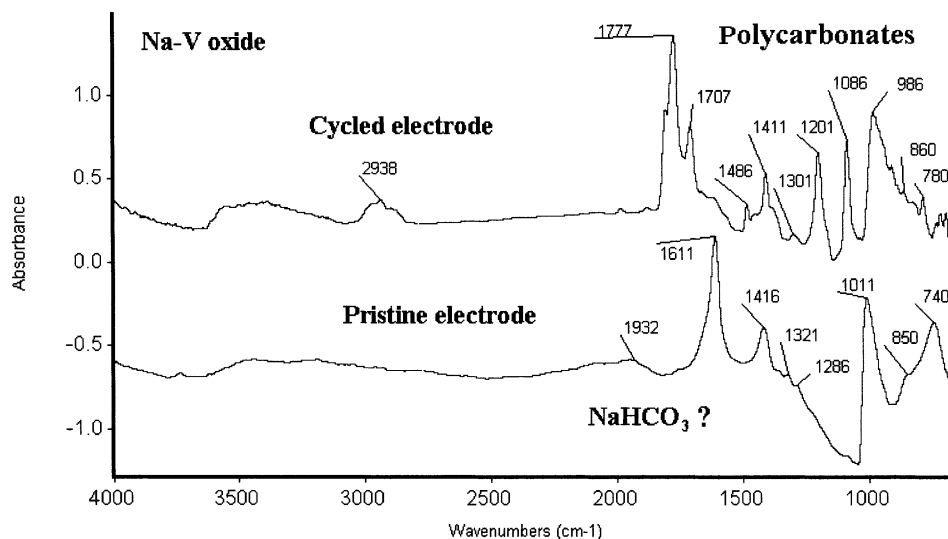


Fig. 4. FTIR spectra measured from pristine and cycled sodium–vanadium oxide electrodes. EC:DMC (1:3)/LiAsF₆ 1 M solution.

sodium bicarbonate and carbonate. As is evident from the spectra in Fig. 4, upon cycling, the surface chemistry of these electrodes undergoes considerable changes, resulting in the formation of polycarbonates (peaks at 1707 and 1777 cm⁻¹), probably due to polymerization of ethylene carbonate. Several pronounced bands located at 1100–1000 cm⁻¹ and 1480–1400 cm⁻¹ can also be attributed to such surface species. Hence, we conclude that the initial surface layers comprised of sodium carbonate and bicarbonate on the sodium–vanadium oxide, are replaced with protective and more resistive layers of EC derivatives (e.g. polycarbonate species). This may result in an increase in the electrode's impedance during cycling, as indeed demonstrated in Fig. 3.

It appears from the above EIS data that, at some states-of-discharge, the impedance spectra of the cathodes include a pronounced 'Warburg'-type element, which relates to the solid state diffusion of Li in the host lattice. The chemical diffusion coefficient D of lithium into the cathode was calculated from the impedance spectroscopy data according to the following formulae [11]

$$D = \left(\frac{l}{A_W \sqrt{2}} \frac{dE}{dQ} \right)^2,$$

where A_W is the Warburg slope defined as $dZ'/d(2\pi f)^{-1/2} = dZ''/d(2\pi f)^{-1/2}$; Z' , Z'' are the real and imaginary components of the impedance, f the frequency, l the diffusion length approximated by the thickness of the sodium–vanadium oxide film (3 μm) and dE/dQ is approximately equal to l/v (v is the potential scan rate). It was important to note that the values of D versus E calculated from EIS (Fig. 2b) were similar to those calculated from potentiostatic intermittent titration (PITT).

Using PITT, the diffusion coefficient was calculated from the Cottrell region of the $It^{1/2}$ versus t or $\log t$ plot (obtained

as a result of incremental potential steps applied to the Li_xNa_yV₂O₅ electrodes), according to the equation [12,13]: $D = [(It^{1/2}l\pi^{1/2})/\Delta Q]^2$. Here, ΔQ denotes the total charge involved during a specific potential step.

It should be mentioned that the chemical diffusion coefficient of Li-ions obtained in the present work are close to the D values for lithium insertion into V₂O₅ based cathodes, reported recently by Kawakita et al. [14].

The steep line in the Nyquist plots at the very low frequencies (Fig. 3) reflects a nearly capacitive behavior related to the accumulation of Li-ions in the bulk. The intercalation capacity of the electrodes, C_{int} , can be calculated from this part of the impedance spectra at the very low frequencies: $C_{\text{int}} = 1/Z''\omega$, $\omega \rightarrow 0$. In all cases we found that the shape of the C_{int} versus E curves calculated from EIS resembles the corresponding slow scan rate CV curves of the cathodes. These results present important proof for the high resolution of the EIS data obtained.

4. Conclusion

We found that monolithic, thin film Na_yV₂O₅ electrodes, prepared by electrochemical synthesis (from aqueous vanadyl and sodium sulphate solutions), followed by thermal annealing (300°C) are promising cathodes for lithium batteries. These electrodes exhibit relatively fast kinetics, high capacity (>200 mAh/g) and stability upon charge–discharge cycling in commonly used electrolyte solutions for Li-ion batteries (e.g. mixtures of alkyl carbonate solvents and standard Li salts). The electroanalytical characteristics obtained from slow scan rate cyclic voltammetry (SSCV) (C_{int} versus E), EIS (C_{int} versus E , D versus E , surface films and charge-transfer resistance), and PITT (D versus E), definitely prove that these electrodes are stable and retain their high capacity and reversibility upon prolonged cycling.

Due to interactions with CO₂ in the air and solution species (mostly EC and acidic species such as HF), these electrodes develop surface films. This was evident from spectroscopic studies (FTIR and XPS) and EIS. We assume that the surface films play a positive role in the stabilization of these electrodes during prolonged cycling.

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