

Short Communication

Rechargeable lithium batteries based on $\text{Li}_{1+x}\text{V}_3\text{O}_8$ thin films

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Abstract

Low-temperature thin films of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ have been fabricated and tested in LiClO_4 /propylene carbonate–1,2-dimethoxyethane/Li cells. These cells show very good intercalation kinetics, and at 0.4 C discharge rate produce a specific energy of ≈ 110 Wh/kg. The films could be used in microbatteries for electronic devices, and applications requiring more power could also be envisaged.

Keywords: Rechargeable lithium batteries; Thin films; Lithium; Vanadium

1. Introduction

In order to maintain the reliability of miniaturized devices and to reduce the power dissipation in high density memories (CMOS-RAM), localized power for such systems is highly desirable. Therefore, microbatteries need to be integrated into the electronics at chip level. To fabricate microbatteries suitable for this application, it is necessary to prepare thin-film multilayers of battery components using processes compatible with microelectronics technologies.

Thin-film rechargeable solid-state lithium batteries that use lithium intercalation compounds as the positive electrode, metallic lithium as the negative electrode, and liquid or solid electrolytes have been reported [1,2].

Significant progress can be still made in the field of cathodic materials, either in obtaining new materials or in improving the electrochemical performance of the compounds already known.

In contrast to conventional syntheses which often involve only a solid-state reaction at high temperatures, ambient-temperature techniques allow the formation of the active material through a chemical or electrochemical reaction performed in a liquid phase (aqueous or organic medium) [3].

In this work we report on the low-temperature formation of thin-film $\text{Li}_{1+x}\text{V}_3\text{O}_8$ electrodes on different substrates. The influence of the preparation conditions on the electrochemical performance of the cathodic materials will be discussed in terms of morphological and microstructural characteristics.

2. Experimental

Amorphous $\text{Li}_{1+x}\text{V}_3\text{O}_8$ was prepared on the basis of a low-temperature technique in which V_2O_5 is added to an aqueous solution of LiOH as described in Ref. [4]. We thus obtained a gel which will be referred to, in this study, as original material (OM).

Preliminary samples were prepared by just dipping stainless-steel supports in the gel. Then, they were kept at an ambient temperature until water was evaporated. Subsequently, some thin samples were prepared from a highly diluted solution of OM by means of a controlled thermal evaporation.

In another set of experiments, a portion of OM was dried under vacuum at 200 °C to remove the water kept in the layers of the structure, and the powder was dispersed in ethanol. Some thin cathodes were prepared by pouring a few drops of this alcoholic preparation on a graphitized aluminium support. These samples, dried using a controlled hot flow, will be referred to as AS (alcoholic solution).

The film thicknesses were calculated from the weight of the deposit and from its density (3.5 g/cm^3). Thicknesses of about 2 μm were often obtained.

The electrochemical tests were carried out in a glass cell in which a glass-wool separator supported an excess of the solution (1 M LiClO_4 in propylene carbonate (PC)–1,2-dimethoxyethane (DME) 1:1). A polymeric solution, LiClO_4 /PC–ethylene carbonate (EC) supported on polyacrylonitrile (PAN), was also used. Some experiments

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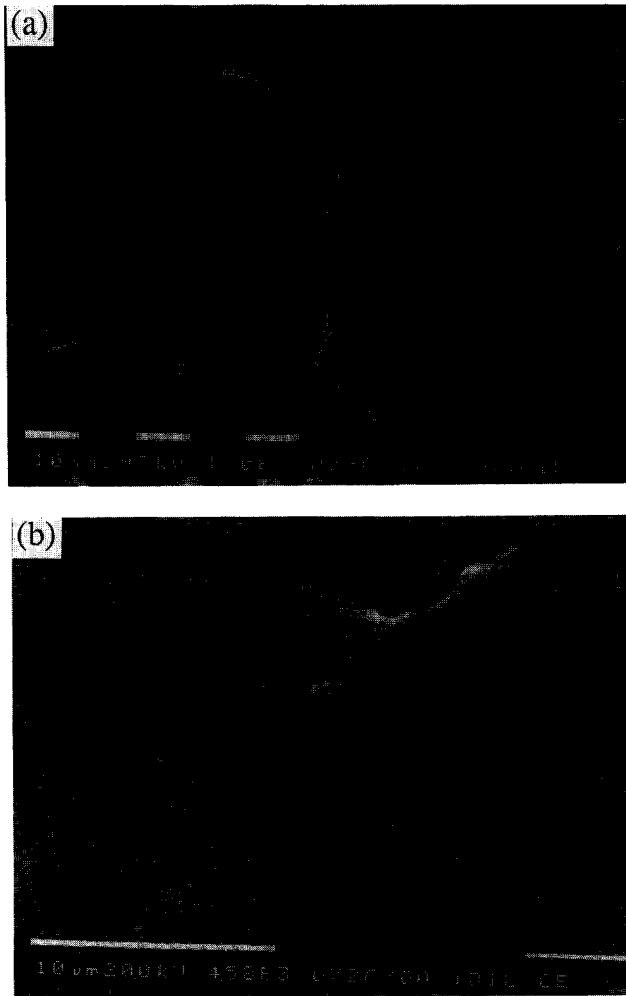


Fig. 1. Scanning electron micrographs of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ on a stainless-steel support: (a) from aqueous gel-like dispersion, and (b) from diluted aqueous dispersion.

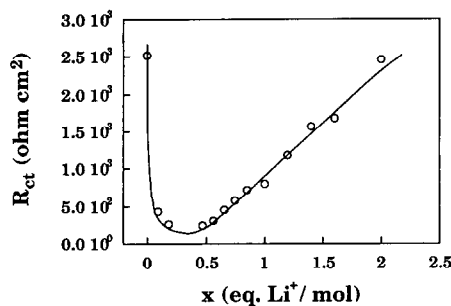


Fig. 2. Charge-transfer resistance at different lithium contents (x) in $\text{Li}_{1+x}\text{V}_3\text{O}_8$ (OM).

required a reference electrode: in this case a lithium rod was inserted in the cell.

All cycles were carried out at a constant current, setting levels of potential or time to reverse the current flow. The charge-transfer resistance (R_{ct}) was measured in a three-electrode cell (Li reference) using a Solartron 1255 impedance analyser in conjunction with a 1286 Solartron electrochemical interface. The frequency ranged from 50 kHz to 100 mHz.

The potential step voltammetry was carried out using the MacPile II computerized system (Biologic). The tests were performed by applying to the cell a potential step of 10 mV/0.5 h and recording the quantity of charge exchanged.

3. Results and discussion

Fig. 1(a) shows the scanning electron micrographs (SEM) of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ (OM) thin layer deposited on a stainless-steel support. This film is uniform in appearance and has a rubber-like consistence. The morphology is different from that previously reported for $\text{Li}_{1+x}\text{V}_3\text{O}_8$ amorphous powder, based on small fluffy particles [4]. Moreover, if one starts from a more dilute solution, a homogeneous featureless film is obtained, as shown in Fig. 1(b). In the latter case, the film was so thin that its weight could not be determined.

Impedance measurements were made on a cathode at various lithium intercalation levels. Fig. 2 reports R_{ct} as a function of composition of the thin films. The initial R_{ct} decrease (up to $x=0.4$ in $\text{Li}_{1+x}\text{V}_3\text{O}_8$) can be attributed tentatively to the limited filling of an empty electron band, while the subsequent increase may be due to its progressive filling [5].

The speed of Li^+ ion diffusion in $\text{Li}_{1+x}\text{V}_3\text{O}_8$ (OM) was measured by impedance tests. From the Warburg straight line, the A_w factor in the equation:

$$|Z_w| = A_w \omega^{-1/2} \quad (1)$$

was calculated with $|Z_w| = \text{Im}Z / \sin \beta$, where $\text{Im}Z$ is the imaginary part of the impedance and β is the angle of the Warburg line with the real axis. From the equation:

$$A_w = \frac{V_m dE/dx}{FAD^{1/2}} \quad (2)$$

where V_m is the molar volume and dE/dx the slope of the coulombmetric titration curve, the chemical diffusion coefficients, D , may be derived [6].

In Fig. 3, the diffusion coefficients of Li^+ in $\text{Li}_{1+x}\text{V}_3\text{O}_8$ are reported. The decrease in D values upon Li^+ ion intercalation correlates with the site occupation which slows down the Li^+ ion mobility. The D values are low and this may be correlated with the residual water in the material, which can limit the Li^+ ion mobility by forming electrostatic bonds. Water is also responsible for the poor specific capacity (see

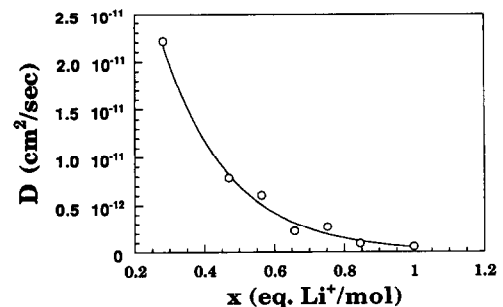


Fig. 3. D_{Li} vs. lithium content (x) in $\text{Li}_{1+x}\text{V}_3\text{O}_8$ (OM).



Fig. 4. Scanning electron micrograph of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ (AS) on graphite aluminium foil.

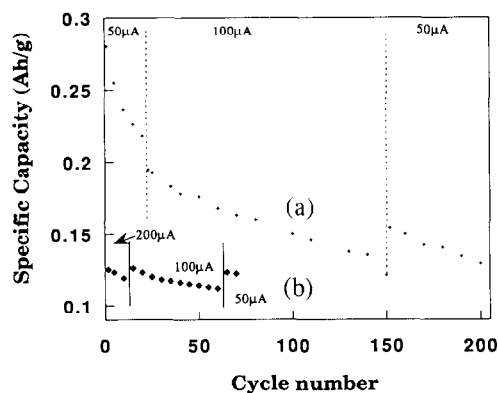


Fig. 5. Specific capacity vs. cycle number for $\text{Li}_{1+x}\text{V}_3\text{O}_8$. Curve (a): AS, and curve (b): OM. Voltage limits = 1.7–3.5 V, and area = 1 cm^2 .

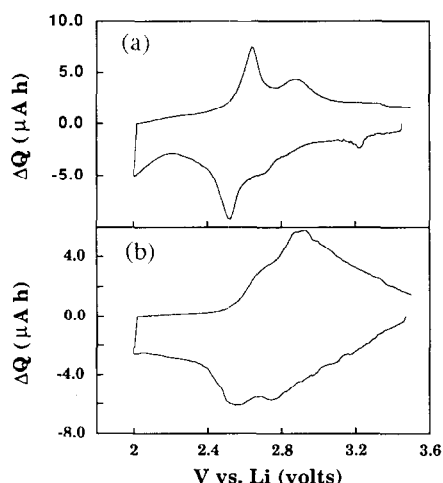


Fig. 6. Potential step spectroscopy of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ samples. (a) AS cathode, and (b) OM cathode. Potential range = 2–3.5 V vs. lithium; potential step $\Delta V = 10 \text{ mV}$, and integration time $\Delta t = 30 \text{ min}$.

later) shown by $\text{Li}_{1+x}\text{V}_3\text{O}_8$ films obtained from an aqueous solution.

Several attempts were made in order to dry the OM films directly on the stainless-steel support. Unfortunately, this

technique cannot be used because the thermal treatment induced the formation of some grooves on the film surface and also produced the detachment of the film from the support. This behaviour may be due to the different thermal capacity and elasticity of the film and its support.

With a view to overcome these difficulties, we prepared several $\text{Li}_{1+x}\text{V}_3\text{O}_8$ films from an alcoholic solution (AS) using a substrate formed by a thin layer of graphite on an aluminium foil. Fig. 4 gives the SEM picture of a $\text{Li}_{1+x}\text{V}_3\text{O}_8$ (AS) deposit. The picture shows a different morphology compared with that obtained with OM.

The cathodic materials prepared from the alcoholic solution exhibited diffusion coefficient values, $D = 3.3 \times 10^{-9} \text{ cm}^2/\text{sec}$, of about two orders of magnitude higher than those found for the samples prepared from the aqueous solution.

A better performance of the samples obtained from the alcoholic solution is shown by cycling experiments. Fig. 5 compares the specific capacity as a function of cycle number for the AS and OM samples. The AS films can sustain many cycles at higher capacity due to the absence of water between its layers.

In order to obtain more information on the reversibility of the redox process of both films, potential-step spectroscopy (PSS) was carried out. Fig. 6(a) shows the AS spectrum. The behaviour reveals that the deposit has a partially crystalline structure, as one might also have suggested from the SEM picture (Fig. 4) [7]. This is probably due to the formation of some local nucleation centres in the material during the drying process. Indeed, different reduction regions are evident. At the beginning, the Li^+ ions occupy the tetrahedral sites of the unit cell [8]. This intercalation process, which is signalled by the peaks at 3.2, 2.8 and 2.7 V, corresponds to different energetic configurations in a single-phase reaction [8]. On the other hand, the peak at 2.52 V is related to the filling of the octahedral sites formed upon intercalation. During this process, two phases coexist [8].

PSS tests on OM films reveal a smoothing of the site energies. The curve of Fig. 6(b) shows that the presence of water in the structure induces the insertion of lithium in two sites of different, but close, energy contents.

Fig. 7 gives the first galvanostatic cycles of AS and OM films at $50 \mu\text{A}/\text{cm}^2$. This Figure points out again that the absence of water between layers in the AS samples allows a higher lithium insertion to be obtained. Also, the charge/discharge process occurring in the AS films takes place with lower polarization, due to its higher D values.

The satisfactory results of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ thin films in rechargeable liquid-electrolyte lithium cells suggested their application in polymeric electrolytes to be used at room temperature [9]. Some preliminary results with $\text{LiClO}_4/\text{PC-EC}$ supported on PAN matrix have been obtained. Fig. 8 shows the specific capacity versus cycle number at different current densities. The results testify that the cells can sustain many cycles in this polymeric electrolyte. From this Figure, it may be also noted that the AS cell shows satisfactory capacities even under severe current-density conditions. Indeed, values

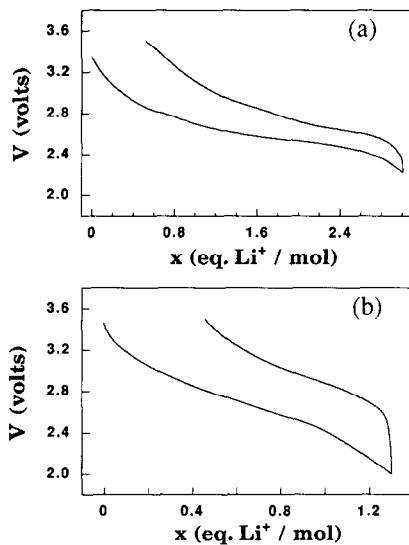


Fig. 7. First galvanostatic discharge of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ cathodes: (a) AS cathode, and (b) OM cathode. Current density = $50 \mu\text{A}/\text{cm}^2$, and voltage limits = 2–3.5 V.

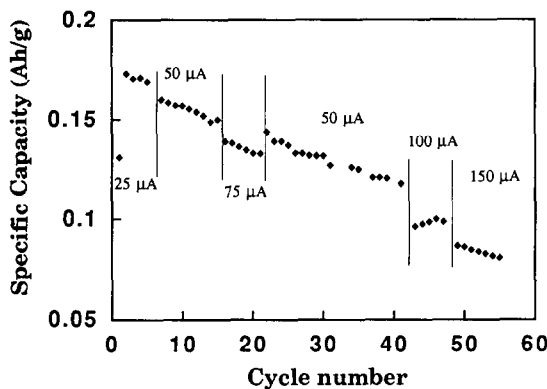


Fig. 8. Specific capacity vs. cycle number for $\text{Li}_{1+x}\text{V}_3\text{O}_8$ AS in polymeric electrolyte. Voltage limits = 2–3.5 V, and area = 1 cm^2 .

ranging from 0.1 to 0.084 Ah/g were obtained with current densities between $100 \mu\text{A}$ and $150 \mu\text{A}$ (118 and 176 mA/g, respectively).

In Fig. 9, the behaviour of the system in terms of specific power and energy characteristics (Ragone plot) is summarized. The slope of the curve is relatively small, allowing to have sufficient power also at medium-high energies. On the basis of these results, $\text{Li}_{1+x}\text{V}_3\text{O}_8$ thin films may be considered as a useful cathode material for practical applications in rechargeable lithium cells, also in association with a polymeric electrolyte. It might be applied not only in the area of consumer electronics but also, in view of its rate capability, in areas where power is required, e.g., electric vehicles.

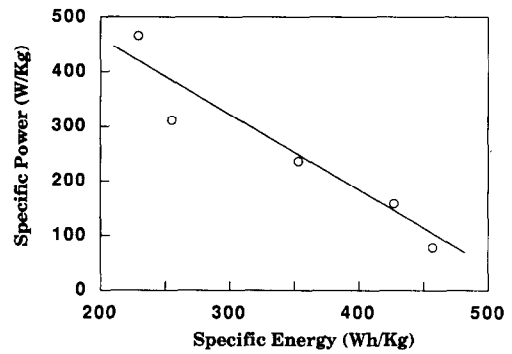


Fig. 9. Ragone plot of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ AS with a polymeric electrolyte.

4. Conclusions

$\text{Li}_{1+x}\text{V}_3\text{O}_8$ thin films prepared by a solution technique show high capacity and fast kinetics in liquid organic electrolytes.

Preliminary experiments in a cell containing a polymeric electrolyte show that an interesting cycling behaviour may also be achieved in this medium. More work on $\text{Li}_{1+x}\text{V}_3\text{O}_8$ thin films, and their use in rechargeable lithium cells, is in progress.

Acknowledgements

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