

Further electrochemical studies on Li/LiV₂O₄ secondary cells

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Abstract

Electrochemical tests on the spinel Li[V₂]O₄ were carried out in lithium cells. The recharge efficiency was measured for $x \leq 2.1$ in 'Li_{1+x}V₂O₄' where 'Li_{1+x}V₂O₄' refers to the overall composition of the working electrode and not necessarily to a single-phase product; the efficiency amounts to 80–85% for compositions ranging between $0.5 \leq x \leq 1.8$. A cycling experiment carried out at the C/2 rate in prototype lithium cells showed that an almost constant capacity of ~ 0.10 A h g⁻¹ could be sustained for nearly 500 cycles, using voltage limits of 1.8 V and 3.0 V. A cell cycled at -10 °C at the C/4 rate delivered a constant capacity of ~ 0.08 A h g⁻¹ over 75 cycles; this corresponds to 73% of the ambient temperature performance.

Introduction

Over the past few years, several studies have focused on the ambient temperature topochemical reactions of lithium with several oxo-spinels in view of their possible application in primary or secondary lithium cells [1]. The isomorphous group of spinels Li[M₂]O₄, where M = Ti, V, Mn, was selected as particularly attractive compounds for positive electrodes for secondary systems, since lithium can not only be inserted into, but can also be extracted from, these spinels, thereby extending their electrode capacity. These compounds are characterised by a cubic normal spinel structure, which has prototypic symmetry $Fd\bar{3}m$ (O_h^7); the anions form a cubic-close-packed array and occupy the 32e sites. The lithium cations reside in one-eighth of the tetrahedral sites (8a), while the transition metal cations occupy one-half of the octahedral sites (16d). Lithium ions can diffuse through the 8a tetrahedra and the 16c octahedra of the interstitial space of the [M₂]O₄ sublattice. Li⁺-ion diffusion has been shown to be faster in the lithium spinels Li[M₂]O₄ (M = Mn, Ti, V) than in spinels where the A site is occupied by relatively heavy transition metal cations [2].

Previous studies of the topochemical reactions of lithium with the spinel (Li)_{8a}[V₂]O₄ showed that lithiation is possible up to at least the composition

$\{\text{Li}_2\}_{16c}[\text{V}_2]\text{O}_4$, while retaining the spinel $[\text{B}_2]\text{X}_4$ framework; lithium extraction was also carried out, but resulted in an irreversible structural change due to vanadium-ion migration within the structure [3]. Preliminary investigations have shown that the system ' $\text{Li}_{1+x}\text{V}_2\text{O}_4$ ' exhibits promising electrochemical properties as an electrode for secondary lithium cells [2, 4].

In particular, $\text{Li}[\text{V}_2]\text{O}_4$ can be lithiated up to at least the composition $x=1$ in $\text{Li}_{1+x}[\text{V}_2]\text{O}_4$, with a load voltage of 2.36 V at low currents [1]. The reversibility of the lithium insertion reaction has been demonstrated by cyclic voltammetry [2]. The reaction is diffusion-controlled [2, 4]; the diffusion rate increases as lithiation proceeds, reaching a value of $D=10^{-8} \text{ cm}^2 \text{ s}^{-1}$ in $\text{Li}_2[\text{V}_2]\text{O}_4$. Cell cycling tests have shown that the system $\text{Li}_{1+x}[\text{V}_2]\text{O}_4$ can be cycled in a lithium cell over ~ 200 cycles with an attractive energy density.

In this work we report further electrochemical data to evaluate the performance of the ' $\text{Li}_{1+x}\text{V}_2\text{O}_4$ ' electrode in a secondary lithium cell for an extended range of x , with $x \leq 2.1$.

Experimental

The $\text{Li}[\text{V}_2]\text{O}_4$ spinel precursor was prepared by a method given previously [5]. Electrochemical tests were carried out in prismatic cells which have been described elsewhere [6]. The active material was mixed with a 30% blend of Teflon and acetylene black (TAB) in a 1:2 ratio using the wet mixing technique reported in a previous paper [4]. This method was found to be advantageous compared with the dry mixing technique, as higher capacities could be obtained, particularly when using faster discharge rates. The electrodes contained ~ 20 mg of active material pressed on a nickel gauze disc with an area of 0.87 cm^2 . The electrolyte chosen for ambient temperature studies was 1.5 M LiAsF_6 in propylene carbonate (PC):methyl formate (MF) (1:1). Cycling at -10°C was carried out using the same electrolyte, but with a PC:MF ratio of 1:3 in order to reduce the electrolyte viscosity. The electrolyte components were dried and purified using standard techniques, and the cells were assembled and discharged under an argon atmosphere.

Recharge efficiency tests were carried out at a charge current density of 0.3 mA cm^{-2} up to a cut-off voltage of 3.1 V in all cases except for the extensively lithiated sample, which was recharged at a current density of 0.1 mA cm^{-2} . The latter was obtained by discharging at 0.1 mA cm^{-2} to 1.3 V, where electrolyte decomposition is negligible, and allowing the potential to rise on open-circuit before continuing the discharge. The procedure was repeated until no further capacity could be extracted from the cell. A blank electrode containing only TAB delivered a negligible capacity (viz., $0.0033 \text{ A h g}^{-1}$) when discharged under the same conditions. Powder X-ray diffraction patterns of the cathodes were recorded with a Philips diffractometer after allowing cells to equilibrate fully on open-circuit.

For comparison, a few samples were lithiated chemically with a strong reducing agent; $\text{Li}[\text{V}_2]\text{O}_4$ was treated with a freshly prepared solution of

lithium naphthalide in tetrahydrofuran (THF). The mixture was stirred for several hours at ambient temperature under an argon atmosphere. The resulting solid material was finally washed repeatedly with THF. The lithium content of these samples was determined by atomic absorption analysis.

Results and discussion

A previous study has shown that good cyclability could be obtained by careful control of the voltage limits; the cell capacity was observed to decrease during cycling when the voltage limits were extended below 1.8 V or above 3.0 V [4]. In this work, the recharge efficiency was determined as a function of depth of discharge; up to 2.1 lithium cations were reacted with $\text{Li}[\text{V}_2]\text{O}_4$ in order to determine optimum cycling conditions (Fig. 1). For low lithium insertion ($x=0.2$ in $\text{Li}_{1+x}[\text{V}_2]\text{O}_4$), the recharge efficiency amounts to only $\sim 55\%$. It increases sharply to 80% for $x=0.5$ and reaches its maximum value ($\sim 85\%$) around $x=1.0$. The increase in efficiency observed for $x \geq 0.5$ could be due to structural modifications which occur in the course of the lithium insertion reaction. It has been shown by powder X-ray diffraction that Li^+ ions migrate from the tetrahedral 8a sites to 16c octahedra at approximately this composition [3]. Additional evidence of this is provided by the variation of the lithium ion diffusion rate as a function of lithium content, which exhibits a discontinuity at $x > 0.6$ [2]. Furthermore, increased voltage during the second discharge, and a change in the shape of the cyclic voltammogram after the first reduction also indicated an irreversible modification of the spinel structure [2, 4]. It has been suggested previously that a small amount of inserted Li^+ ions stabilises the structure [4]. The recharge efficiency remains almost constant between $0.9 \leq x \leq 1.8$; it then drops sharply, reaching a value of $\sim 30\%$ for $x=2.1$.

The structural characteristics of samples ' $\text{Li}_{1+x}\text{V}_2\text{O}_4$ ' where $1 < x < 2.1$ are not fully understood. If the nature of the reaction is topochemical, face-sharing octahedra and tetrahedra would necessarily have to be filled. This has previously been observed in the cases of $\text{Li}_{1.5}[\text{V}_2]\text{O}_4$ [3] and $\text{Li}_2[\text{Mn}_2]\text{O}_4$ [7, 8]. Although, *a priori*, this configuration would seem energetically

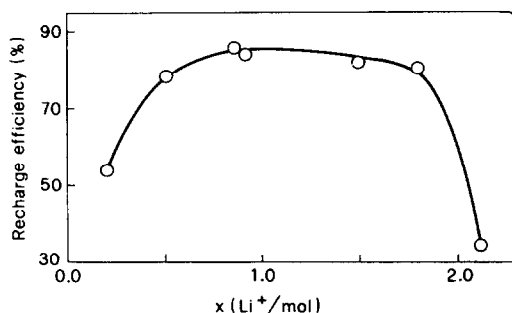


Fig. 1. First recharge efficiency shown as a function of the depth of discharge, x , in ' $\text{Li}_{1+x}\text{V}_2\text{O}_4$ '.

unfavourable, lithium-ion pair formation has been suggested as a possible stabilisation mechanism [9]. X-ray diffraction patterns of the discharged 'Li_{1+x}V₂O₄' electrodes are characteristic of a cubic spinel: an increase of the cell constant is observed in samples with a higher lithium content, confirming previous reports [9, 10]. The quality of the data was, unfortunately, too low to allow a complete structure determination, since the electrodes consisted of a very limited amount of active material, mixed with diluents and supported on gauze, which could have impaired the smoothness of the surface. Chemical lithiation reactions, using a strong lithiating reagent such as lithium naphthalide, were therefore carried out in order to prepare large samples of a similar composition. Despite the fact that lithium naphthalide has a reduction potential of 0.5 V, in contrast to 1.0 V for *n*-BuLi [11], samples with a lithium content $x > 1.2$ in 'Li_{1+x}V₂O₄' could not be obtained. Although this is a surprising result in view of the strong reducing power of lithium naphthalide, electrochemical reactions have often been shown to be more effective than chemical routes, thanks to the better kinetic control they afford at low rates.

Lithium insertion beyond $x = 1$ has previously been observed in a number of spinels: in-depth structural investigations of these products have usually revealed significant structural changes in the host compound. Upon prolonged reaction with *n*-BuLi at 50 °C, the isomorphous spinel Li[Mn₂]O₄ can be converted to Li₄Mn₂O₄: this compound, however, has an hexagonally-close-packed anion sub-array in which the cations Li⁺ and Mn²⁺ are distributed in alternate layers and occupy tetrahedral and octahedral sites, respectively [12]. Co²⁺[Co₂³⁺]O₄ forms a rocksalt-type compound {LiCo}_{16c}[Co₂]_{16d}O₄; further reaction yields a two-phase product comprising a rocksalt phase, Li_{1+y}Co_{3-y}O₄, where $0 < y < 1$, and metallic cobalt, which was probably extruded from the 16d octahedra [13]. Under selected conditions, the defect thiospinel In₂S₃ has been observed to react with 6 equivalents of lithium per unit of In_{0.67}[In₂]S₄; the spinel framework was retained in the course of extensive reaction with lithium, but powder X-ray diffraction patterns of some products clearly evidenced the presence of reduced indium metal [14]. The expulsion of the A-site metal cation has been shown to accompany the insertion of two Li⁺ ions into a large number of thio-spinels and seleno-spinels; these reactions yield a rocksalt structure {Li₂}_{16c}[B₂]_{16d}S₄ (for example, where B = Zr, Yb) [15, 16]. Ambient temperature lithium insertion into α-Fe₂O₃ occurs via a defect rocksalt phase and proceeds to a composition Li_{1.7}Fe₂O₃; the mechanism is similar to that observed when magnetite is lithiated to a composition Li_{1.5}Fe₃O₄ [17]. The single-phase powder-X-ray-diffraction pattern, which indexes to a rocksalt structure, would suggest that all the octahedral, and part of the tetrahedral, sites are filled. Recent Mössbauer measurements, however, have shown that the product comprises several phases, one of which is Fe⁰ [18]. Greenblatt and co-workers have reported the insertion of two lithium cations per spinel formula unit in Fe[Li_{0.5}Fe_{1.5}]O₄, Fe[NiFe]O₄ and Zn[Co₂]O₄: a lithium content of $1.2 \leq x \leq 1.5$ was achieved in Fe_{0.5}Zn_{0.5}[Fe₂]O₄, Zn[MnFe]O₄ and MnFe₂O₄ (in which the manganese and

iron cations are distributed between the A tetrahedra and the B octahedra) [19–21]. It is worth noting that in all the compounds where two lithium cations were inserted, either iron or cobalt cations were present on the A or B sites and could have been extruded as in $\text{Li}_x\text{Fe}_2\text{O}_3$ and $\text{Li}_x\text{Co}_3\text{O}_4$ for $x > 1$.

Although the X-ray patterns of ' $\text{Li}_{1+x}\text{V}_2\text{O}_4$ ' ($1 < x < 2.1$) appear to be single-phase, the presence of other phases cannot be excluded. There is no evidence of the formation of a compound isostructural with $\text{Li}_4\text{Mn}_2\text{O}_4$. The extrusion of vanadium metal seems unlikely: the theoretical voltage for the reduction of V^{3+} or V^{2+} to the metallic state in a lithium cell is below 1 V [22]. For comparison, the theoretical voltage values at 298 K for the reduction of the Fe^{2+} and Co^{2+} ions are 1.65 V and 1.83 V, respectively [22]. The formation of ' $\text{Li}_2\text{O}\cdot\text{VO}_y$ ' at the particle surface, where the Li^+ -ion concentration is highest, could be envisaged. This metastable phase may then decompose slowly during the long equilibration times. The formation of the oxide VO_y , which is known to have a rocksalt structure for $0.7 \leq y \leq 1.4$, with a cell constant $4.03 \text{ \AA} \leq a \leq 4.14 \text{ \AA}$ [23], cannot be excluded because, for $x = 2$ in ' $\text{Li}_{1+x}\text{V}_2\text{O}_4$ ', the average vanadium oxidation state is 2.5. The decrease in recharge efficiency for $x > 1.8$ can probably be attributed to a disproportionation reaction of the type suggested above.

A preliminary evaluation of the performance of the $\text{Li}[\text{V}_2]\text{O}_4$ spinel electrode during cell cycling showed that, after a few cycles, an almost constant capacity (viz., $\sim 0.10 \text{ A h g}^{-1}$) could be obtained over ~ 200 cycles at a rate of $C/9$ or $C/4.5$, using voltage limits of 1.8 V and 3.0 V. A capacity loss was observed when a wider voltage range was used. At a higher rate ($C/1.8$) the capacity initially decreased considerably, but stabilised at $\sim 0.09 \text{ A h g}^{-1}$ after 30 cycles [4].

In this work, the electrode homogeneity was improved using the wet mixing technique [4]. An LiAsF_6 -PC/MF solution was selected as an electrolyte, because parallel tests showed that, for $\text{Li}/\text{Li}_{1+x}\text{V}_2\text{O}_4$ cells, a higher utilisation could be obtained compared with that observed with the LiClO_4 -PC/DME solution used previously [4]. Voltage limits were set at 1.8 V and 3.0 V; cycling was carried out at a current density of 1 mA cm^{-2} , which was equivalent to a $C/2$ rate using the $1 \text{ Li}^+ \text{ mol}^{-1}$ reaction to calculate the theoretical capacity. In the course of the first discharge $0.75 \text{ Li}^+ \text{ mol}^{-1}$ were inserted, corresponding to a capacity of 0.115 A h g^{-1} . The capacity dropped gradually in the first 150 cycles to $\sim 85\%$ of the first discharge and then stabilised just below 0.10 A h g^{-1} ; the cell exhibited limited capacity loss over the following 300 cycles (Fig. 2). Failure of the cell after 500 cycles was partly due to the degradation of the lithium anode which reacted with the electrolyte, forming a thick brown film: improved cyclability of the negative electrode is widely acknowledged to be a major goal in the development of secondary lithium batteries. At the end of the test, the cathode was X-rayed and compared with the starting material, $\text{Li}[\text{V}_2]\text{O}_4$. As is evident in Fig. 3, the spinel structure is retained. An unidentified peak appears at $d = 3.10 \text{ \AA}$. The lattice constant increased to $a = 8.32(1) \text{ \AA}$, indicating a 3% expansion

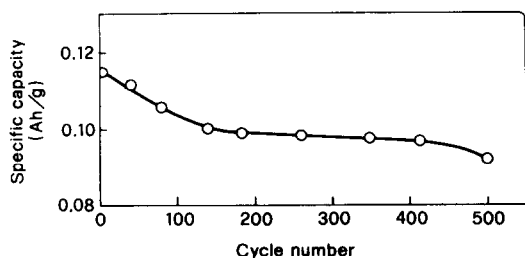


Fig. 2. Specific capacity as a function of the cycle number at the $C/2$ rate.

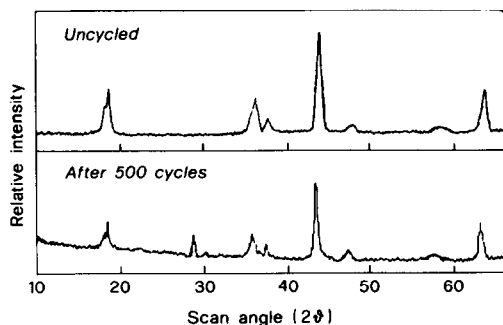


Fig. 3. Powder X-ray diffraction pattern of (a) LiV_2O_4 and (b) an electrode in the charged state after 500 cycles.

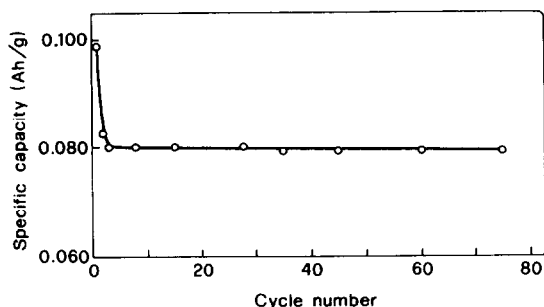


Fig. 4. Specific capacity as a function of the cycle number at the $C/4$ rate at low temperature.

of the cell volume: this is a greater increase than that observed when the spinel is lithiated to form $\text{Li}_2[\text{V}_2]\text{O}_4$ [3].

A low-temperature cycling test was undertaken at -10°C at a current density of 0.5 mA cm^{-2} ($C/4$). Within the first three cycles, the capacity dropped from 0.10 A h g^{-1} to 0.08 A h g^{-1} ; it remained stable at this value up to cycle 75 (Fig. 4). At this point the electrode delivered $\sim 73\%$ of the capacity obtained at ambient temperature. This indicates that the system ' $\text{Li}_{1+x}\text{V}_2\text{O}_4$ ' performs relatively well at low temperature, notwithstanding the fact that the measurements were carried out at different current densities.

For comparison, the capacity of a commercial primary Li/MnO₂ button cell drops by 14% when the temperature is lowered from 20 °C to -10 °C [24].

Conclusions

The results presented in this paper confirm that the spinel system 'Li_{1+x}V₂O₄' offers good cyclability in secondary lithium cells: ~0.6 Li⁺ ions can be reversibly inserted over ~450 cycles. With an average voltage of 2.25 V, the energy density obtained after more than 400 cycles is ~220 W h kg⁻¹; this figure is similar to the value obtained in commercial rechargeable Li/MoS₂ cells (230 W h kg⁻¹) based on the reaction of 0.8 Li⁺ mol⁻¹ [25]. Recent experiments carried out under the conditions reported here, have shown that only 0.4–0.45 Li⁺ ions can be reversibly inserted into the spinel Li_{1+x}[Mn₂]O₄ at 1 mA cm⁻². This result is in agreement with data by Sanyo [26], while a better utilization is claimed in a patent by Sony [27].

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