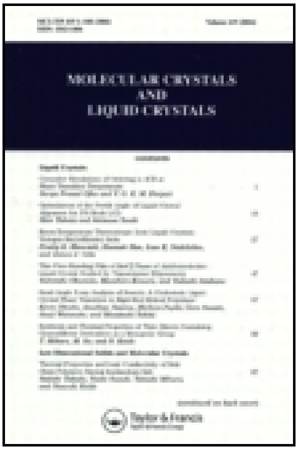


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Electrochemical Properties vs. Li of Amorphous/Crystallized Indium Vanadates

S. Denis [a] , E. Baudrin [a] , M. Touboul [a] & J-M. Tarascon [a]

[a] Laboratoire de Réactivité et de Chimie des Solides, UPRES A 6007, U.P.J.V., 33 rue Saint-Leu, 80039, Amiens Cedex, France

To cite this article: S. Denis, E. Baudrin, M. Touboul & J-M. Tarascon (1998): Synthesis and Electrochemical Properties vs. Li of Amorphous/Crystallized Indium Vanadates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 311:1, 351-357

To link to this article: http://dx.doi.org/10.1080/10587259808042410

Mol. Cryst. Liq. Cryst., 1998, Vol. 311, pp. 351-357
Reprints available directly from the publisher
Photocopying permitted by license only

Synthesis and Electrochemical Properties vs. Li of Amorphous / Crystallized Indium Vanadates

S. Denis, E. Baudrin, M. Touboul and J-M. Tarascon.
Laboratoire de Réactivité et de Chimie des Solides, UPRES A 6007, U.P.J.V., 33 rue Saint-Leu, 80039 Amiens Cedex, France.

Abstract

A dissolution-reprecipitation process from a mixed solution of NH_4VO_3 and $In(NO_3)_3$ is described for the low-temperature preparation of amorphous $InVO_4{\cdot}2.3H_2O$. Crystallized phases were obtained depending on the annealing temperature of amorphous $InVO_4{\cdot}2.3H_2O$. An electrochemical investigation has shown that these compounds, depending on their amorphous/crystallized nature, can react with large amounts of Li, leading to reversible capacities as large as 900 mA-h/g. Both electrochemical and in-situ X-ray diffraction studies suggest that a mechanism of Li uptake/removal, different from the usual Li insertion/deinsertion process, is occurring in these vanadates.

Introduction

In the search for better negative electrodes, researchers have been trying to improve the reversible capacity of carbonaceous materials either by pyrolysis of organic molecules[1] or by mechanical grinding[2]. Idota[3] has recently opened new avenues of research towards this goal by showing that several Li-vanadates based electrodes, when discharged to voltages lower than 0.2 V, can reversibly intercalate up to 7 Li leading to 800-900 A-h/Kg capacities, about two and a half times greater than present graphite electrodes. These reported crystallized vanadates[3,4] were, however, shown to become amorphous during the first discharge reduction. So it was interesting to prepare these materials in the amorphous state in a first place.

Presently, mixed crystallized vanadates fabrication requires calcination and annealing at temperatures greater than 500°C for a few days. Herein, we report through the use of a dissolution-reprecipitation process the ability to prepare amorphous indium vanadates. An electrochemical study of these compounds, either amorphous or crystallized, has revealed for some of them their potential interest as negative electrodes in lithium-ion rechargeable batteries. For instance, $InVO_4{\cdot}2.3H_2O$ displays a reversible capacity as large as 900 mA-h/g.

Experimental

Electrochemical measurements were carried out on Swagelok™ laboratory test cells by means of a "Mac-Pile" system (Biologic S.A., Claix, France). These cells were built using $InVO_4$ as the active positive electrode material and Li metal as the active negative electrode material. The plastic positive electrode laminate was made using Bellcore's plastic LiION technology. A 1 M $LiPF_6$ 1/3 DMC and 2/3 EC (weight ratio) solution was used as the electrolyte for all the electrochemical measurements reported herein.

The in-situ X-ray diffraction measurements were performed on a Siemens D5000 diffractometer (using the Cu $K\alpha_1$ radiation $\lambda=1.5406$ Å) connected to a Mac-Pile system for in-situ testing. An in-situ electrochemical cell, whose design is described elsewhere[5], was used for these measurements. The cell was discharged and charged through a galvanostatic mode at very low current rates (e.g. = C/200) in order to be close to equilibrium conditions.

Synthesis, thermal properties of amorphous $InVO_4$

1- Synthesis

The synthesis method[6] consists in mixing a NH_4VO_3 solution with a $In(NO_3)_3$ solution in the stoichiometric amounts. Upon mixing, a partial and inhomogeneous precipitation (pH=2.4) occurs instantaneously. To ensure a complete and homogeneous reaction, the precipitate is first dissolved by lowering the pH of the solution to about 1. The pH is then raised to about 3.5 to favor the precipitation. Afterwards, the mixture is stirred and heated at 50°C for 15 minutes. The precipitate is then separated from the solution by centrifugation and washed with water and acetone several times to ensure complete ammonium nitrate removal. The precipitate, dried overnight at 50°C, is amorphous as determined by X-ray diffraction measurements.

2- Thermal properties

The thermal stability of this vanadate was investigated by annealing $InVO_4{\cdot}nH_2O$ under argon flow during 15 hours from 200 to 700°C by steps of 100°C. Until 400°C, the XRD patterns were found to be featureless indicating the amorphous nature of the powders. At 500°C, the amorphous compound crystallizes in the monoclinic $InVO4$ form[7], which in turn converts progressively to the orthorhombic InVO4 phase[8] when the annealing temperature reaches 600°C.

Thermal analyses performed on the amorphous compound have respectively indicated the loss of 2.3 water molecules per formula unit (which corresponds both to adsorbed and structural water molecules) and confirmed the crystallization of the amorphous phase around 500°C in a monoclinic form and the monoclinic-orthorhombic transformation around 700°C.

Electrochemical results and discussion

1- amorphous and crystallized InVO$_4$

Fig. 1 shows the voltage versus lithium content curves for (a) amorphous (dried at 50°C) and (b) monoclinic and (c) orthorhombic InVO$_4$ samples (obtained by annealing (a) at 500°C and 700°C for 15 hours respectively).

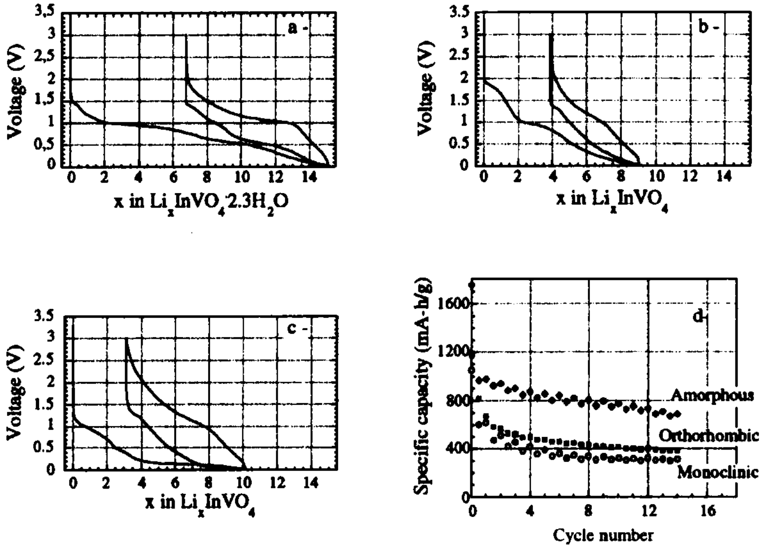


Fig. 1: Voltage vs. composition profile curves for a) amorphous InVO$_4$·2.3H$_2$O, b) monoclinic and c) orthorhombic InVO$_4$. d) represents their cycling behavior. A rate of 1Li/100 min was used over the 0.02-3V voltage range.

Amorphous InVO$_4$·2.3H$_2$O can react reversibly with about 8 lithium ions per formula unit, resulting in capacities as large as 900 mA-h/g (e.g. two times greater than those obtained with conventional graphite electrodes), while monoclinic and orthorhombic $InVO_4$ can react with only 5 and 7 lithiums per formula unit, respectively. However, the irreversible capacity is larger for the amorphous than for the crystallized phases, as expected as the result of the BET surface areas (55, 22 and 4 m^2/g, respectively). The amount of adsorbed water contained in the amorphous phase has also to be taken into account to explain in part the large irreversible capacity loss for this material.

Fig. 1d shows that batteries based on amorphous rather than crystallized $InVO_4$ as the positive electrode display a better capacity retention upon cycling, emphasizing the advantage of having an amorphous phase. Indeed, after 14 cycles, the amorphous phase still sustains a capacity of about 700 mA-h/g, compared to about 300-400 mA-h/g for the monoclinic and orthorhombic $InVO_4$ phases, respectively.

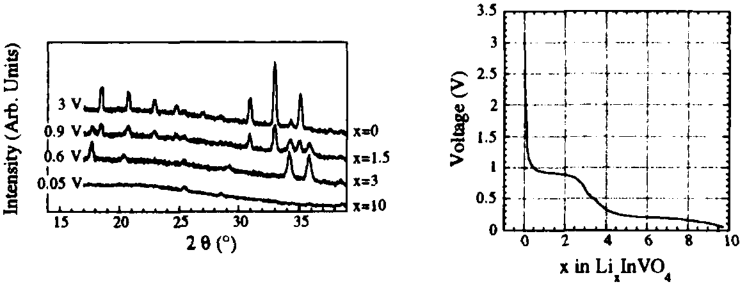
2- *In-situ X-ray diffraction*

As an attempt to throw some light on the Li reaction mechanism within $InVO_4$, in-situ X-ray diffraction measurements starting from orthorhombic and monoclinic $InVO_4$ were performed.

a) orthorhombic $InVO_4$

A cell using orthorhombic $InVO_4$ as the cathode material was discharged to 0.02 V at a constant current rate (0.032 mA corresponding to 1Li/20h), and then charged to 3 V. XRD patterns were taken approximately every 0.25 lithium introduced or removed. The most significant XRD patterns are shown in Fig. 2a.

For $0<x<0.5$, the XRD patterns are characteristic of orthorhombic $InVO_4$[8] without any noticeable differences. Upon further increasing x, for $0.5<x<3$, the peaks corresponding to the original orthorhombic $InVO_4$ phase vanish while the ones corresponding to a new phase (denoted hereafter X) grow, indicating a two phases region. This is consistent with the electrochemical data showing the appearance of a plateau at 0.9 V in the V vs. x curve (Fig. 2b). This new phase is obtained as a single phase at $x=3$. For $x>3$, the diffraction peaks decrease in intensity and broaden so that the XRD diffraction pattern becomes featureless (e.g. characteristic of complete amorphization) for $x=7$. Further reduction down to 0.02 V corresponds to an x of 10 where the lithiated electrode was found to remain amorphous. The XRD patterns of the oxidized vanadate phase collected during the recharge of the in-situ cell up to 3 V were all featureless indicating that the first discharge produced an amorphization of the electrode material that remains on subsequent charge/discharge cycles.



a b

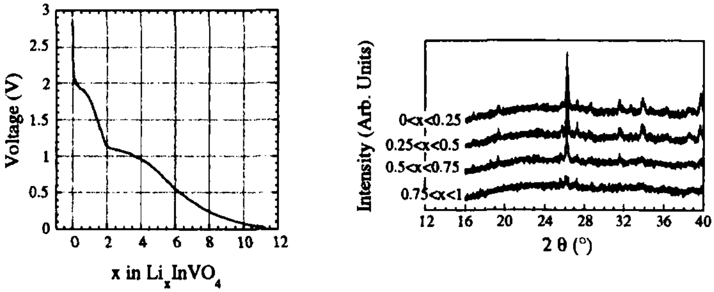
Fig. 2: XRD patterns obtained for an electrochemical in-situ X-ray cell using orthorhombic $InVO_4$ as the positive electrode and Li as the negative electrode (a). Only the most significant XRD patterns taken during the first discharge (b) are shown.

To account for the formation of the X-phase containing 3 inserted lithium ions from the reduction of $InVO_4$ by Li, one could simply suppose that V^{5+} gets reduced to V^{2+} while In remains as a +3 ion. If so, the hypothetical formula Li_3InVO_4 can be proposed for the X-phase. Moreover, discharging orthorhombic $InVO_4$-based electrode to 0.6 V and recharging the cell to 3.5 V do not allow Li removal, so that the transformation of the orthorhombic $InVO_4$ in the X-phase is irreversible. However, further work is needed in order to determine the X-phase formula as well as to solve accurately its structure.

b) monoclinic $InVO_4$

An in-situ X-ray diffraction cell using monoclinic $InVO_4$ as the cathode material was tested in the course of the first discharge to 0.02 V (Fig. 3a) at constant current rate (0.042 mA corresponding to 1Li/20h). XRD patterns were taken approximately every 0.25 lithium introduced. The XRD results are shown in Fig. 3b.

From x=0 to x=0.5, the XRD pattern remains characteristic of pure monoclinic $InVO_4$. In contrast, from x=0.5 to x=1, the relative intensity of the diffraction peaks decreases, and at x=1 the XRD pattern is featureless. The obtained compound was found to remain amorphous until the end of the discharge and then upon subsequent charge/discharge cycles. So, the reaction with Li proceeds quite differently in the two $InVO_4$ forms. Amorphization occurs once the Li-introduction starts in monoclinic $InVO_4$ while a new phase is first formed at x=3 (V=0.9 V), prior to that amorphization occurs for orthorhombic $InVO_4$.



a **b**

Fig. 3: XRD patterns taken during the first discharge (a) of an electrochemical in-situ X-ray cell using monoclinic $InVO_4$ as the positive electrode and Li as the negative electrode. Only the most significant XRD patterns (b) are shown.

Conclusion

We have shown how, by carefully controlling the pH of a dissolution-reprecipitation reaction, we succeeded in preparing pure amorphous indium vanadates and demonstrated the use of this amorphous phase as a precursor to produce crystallized vanadates by annealing treatments. An electrochemical investigation has shown that these compounds, depending on their amorphous/crystallized nature can react with large amounts of Li; for instance 8 lithiums could be inserted per $InVO_4$ formula unit. Based on their electroactive capacity at low potential, some of these phases could be considered as potential negative electrodes for Li-ion batteries. However, a large capacity fading upon cycling was always noted. It will thus be stressed that an understanding of the SEI interface growth on the vanadate upon cycling (e.g. its formation/ dissolution) is a must for such materials to be alternative to graphite negative electrodes in rechargeable Li-ion batteries.

To account for such amount of reacted Li, In^{3+} and V^{5+} will have to be reduced to their metallic state. In-situ X-ray diffraction measurements performed on crystallized indium vanadate phases showed that once lithium was introduced an amorphization of the material during the first discharge occurs, but never give evidence for In^0 or V^0 during the reduction process. These results strongly suggest that a Li uptake/removal mechanism different from the usual Li insertion/deinsertion process should be proposed. However, the phase decomposition evidence during amorphization is the achievement of a Li-V-O type compound upon annealing amorphous oxidized materials that were electrochemically reduced once[9]. Thus, the decomposition of $InVO_4$ must be taken into account in any proposed mechanisms to explain our electrochemical data.

References

1. T. Zheng, J.S. Xue and J.R. Dahn, *Chem. Mater.*, **8**, 383 (1996).
2. F. Disma, L. Aymard, L. Dupont and J-M. Tarascon, *J. Electrochem. Soc.*, **143**, 3959 (1996).
3. Y. Idota, Eur. Patent 0 567 149 A1.
4. C. Sigala, D. Guyomard, Y. Piffard and M. Tournoux, *C.R. Acad. Sci. Paris*, **320 (IIb)**, 523 (1995).
5. G.G. Amatucci, J-M. Tarascon and L.C. Klein, *J. Electrochem. Soc.*, **143** (1996).
6. M. Touboul and A. Popot, *Rev. Chim. Miner.*, **22**, 610 (1985).
7. M. Touboul, K. Melghit and P. Bénard, *Eur. J. Solid State Inorg. Chem.*, **31**, 151 (1994).
8. M. Touboul, K. Melghit and S. Denis, *Powder Diffraction*, **11**, 22 (1996).
9. S. Denis, E. Baudrin, M. Touboul and J-M. Tarascon, *J. Electrochem. Soc.*, in press.