High pressure materials for energy storage. The case of V$_2$O$_5$

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Abstract. The high pressure polymorph of V$_2$O$_5$ is investigated as example of a high-pressure material (HP-V$_2$O$_5$) with potential applications in electrochemical devices, such as lithium batteries. HP-V$_2$O$_5$ reversibly intercalates up to 2 lithium ions down to 1 Volt vs Li$^+/\text{Li}$. The typical voltage-composition profile of HP-V$_2$O$_5$ shows distinct features than that of the ambient pressure polymorph, AP-V$_2$O$_5$. Remarkably, the specific capacity retention with cycling of HP-V$_2$O$_5$ // Li cells (250 Ah/Kg at a C/3.5 rate) is comparable to that of the ambient pressure polymorph. Furthermore, the measured resistivities at room temperature (10000 $\Omega$cm in AP and 400 $\Omega$cm in HP) reveal that HP-V$_2$O$_5$ is a better electronic conductor than AP-V$_2$O$_5$. The enhanced electronic conductivity of HP-V$_2$O$_5$ is an advantage for electrochemical applications.

1. Introduction

New synthesis strategies are needed to prepare novel electrode materials for lithium batteries. High pressure / high temperature routes are widely used within other fields of Solid State Chemistry to induce structural transformations of materials, conducting to novel polymorphs possessing structures not accessible at ambient pressure. However, compounds obtained under high pressure present structures denser than those corresponding to ambient pressure materials, therefore, they have been traditionally ruled out as host materials for insertion reactions. On the other hand, a high pressure polymorph generally presents a better electronic conductivity that the ambient pressure polymorph, which is an advantage in terms of electrochemical applications.

In the last years we have explored the electrochemical application of high-pressure materials [1-3]. V$_2$O$_5$, ranks among the most studied electrode for lithium batteries due to its high energy density and capacity retention upon cycling [4]. Under high pressure (40-80 kbar) V$_2$O$_5$ transforms into a layered polymorph, HP-V$_2$O$_5$, consisting on V$^{5+}$O$_6$ octahedra instead of V$^{5+}$O$_5$-square pyramids (figure 1) [5]. In this contribution we focus on the high-pressure polymorph of V$_2$O$_5$, as an example of a high-pressure material displaying a good performance as positive electrode for lithium batteries.

2. Results and discussion

Commercial (Aldrich) V$_2$O$_5$ was subjected at 4, 6 and 8 GPa and 800 °C for 1 hour in a belt-type press. In-situ synchrotron X-ray diffraction (SXRD) experiments were performed at the B2 line at HASYLAB working in transmission mode, using a cell previously described [6], and radiation of wavelength $\lambda$=0.489646 Å. As detector a scintillation counter with an analysing crystal in front of it for high resolution is used. The treatment of the diffraction data was carried out using the FullProf program [7].
The electrochemical experiments were performed in Swagelok cells using a disk of lithium metal as the negative and reference electrode. As electrolyte we used the commercial solution of LiPF$_6$ in EC (ethylene carbonate) and DMC (dimethyl carbonate) (1:1) Selectipur LP30® (Merck). The positive electrode consisted of a mixture of HP-$V_2$O$_5$, carbon black, and a binder (PVDF-HFP) in a 80:15:5 weight ratio conformed in 8 mm-diameter pellets of about 10 mg. Cell were assembled in a glove-box filled with argon and connected to a MacPile multichannel potentiostat-galvanostat. DC transport measurements in temperature region $77 < T < 300$K have been done in both, 4-contact and 2-contact configurations.

3. Results and discussion

$V_2$O$_5$ treated at 4-8 GPa and 800 ºC turns into a black-reddish powder and, independently of the pressure used in the experiments, the patterns of all the samples can be indexed with the unit cell previously proposed for HP-$V_2$O$_5$ [4] (see Figure 1).

![Figure 1: Graphic result (experimental, calculated and their difference) of the fitting of SXRD data of HP-$V_2$O$_5$; in the inset a schematic representation of its structure is depicted. Peaks from the sample holder (Al) and Li from the electrode are fitted as phase-II and phase-III. Final cell parameters for HP-$V_2$O$_5$ are $a = 7.181(1)$ Å, $b = 3.58747 (7)$ Å, $c = 6.2998 (2)$Å, $\beta = 89.854(7)$, S.G. P21/m. R$_p$: 2.20, R$_{exp}$: 2.93, R$_{exp}$: 0.80, $\chi^2$: 13.3.](image)

Figure 2a compares the Open Circuit Voltage (OCV) measurements of two Li // HP-$V_2$O$_5$ cells using the AP-$V_2$O$_5$ (curve in red) and the HP-$V_2$O$_5$ (curve in green) as active materials. The single phases Li$_x$-$V_2$O$_5$ appear as abrupt voltage drops in the composition curve. Up to six Li$_x$HP-$V_2$O$_5$ single phases are observed, with approximate compositional stability domains of $0 < x < 0.02$, $0.23 < x < 0.26$, $0.56 < x < 0.59$, $0.76 < x < 0.9$, $1.57 < x < 1.65$ and $1.80 < x < 2$. These compositional limits are clearly different from those found on the Li$_x$V$_2$O$_5$ phases derived from the ambient pressure polymorph [4]. In particular, the single phase centred at $x=1$, which is very characteristics of AP-$V_2$O$_5$, is absent in the HP-$V_2$O$_5$. The polarization is of the same order in both cells, suggesting a similar kinetics of the lithium insertion reaction into the AP/HP host materials.
Figure 2. (a) Open circuit voltage of Li//V$_2$O$_5$ cells discharged at j = 0.37 mA/cm$^2$ for 1 h (C/7 rate). Cells were kept at open circuit for 20 hours, or until the variation of voltage with time was lower than 0.01mV/h. (b) Cycling of Li//HP-V$_2$O$_5$ cell in a voltage window 3.8-1V.

Figure 2b shows a typical cycling experiment of a Li // HP-V$_2$O$_5$ cell performed between 1 and 3.8 V under constant current density equivalent to a C/3.5 rate. The specific capacity delivered by the cell is of about 250 Ah/Kg, and remains constant with cycling. Thus, lithium ions can be reversibly inserted / deinserted into / from the high pressure polymorph of V$_2$O$_5$ with almost no capacity fade upon cycling. It should be noticed that HP-V$_2$O$_5$ displays the same reversible capacity than V$_2$O$_5$, though in a somewhat wider voltage range (see figure 2a). It is worth mentioning that none of the characteristic processes of V$_2$O$_5$ was observed in the V-x curves for any of the Li//HP-V$_2$O$_5$ cells studied. This discards an eventual reversion of the phase transformation induced by high pressure.

The electrical conductivity of an electrode material determines the polarization of the positive electrode, thus governing the power rate capability of the lithium cell. The improvement of electronic conductivity is particularly relevant in the case of electrode materials lacking a good electronic conductivity, such as LiFePO$_4$; by means of high pressure it might be possible to modify the electronic structure of a material, presumably improving the electronic conductivity. Hence, in the example under study, it is important to compare the conductivity of the AP/HP V$_2$O$_5$ polymorphs. The d.c. conductivity was measured on both polymorphs of V$_2$O$_5$ from room temperature down to T=77K [8]. As shown in figure 3, the room temperature resistivity decreases by more than one order of magnitude: from 10000 $\Omega$cm in AP-V$_2$O$_5$ to 400 $\Omega$cm in HP-V$_2$O$_5$. In the above temperature window, resistivities of both compounds show activated behavior with activation energies $E_A$ of 0.232 and 0.068 eV for AP and HP polymorphs, respectively. The enhanced electronic conductivity of HP-V$_2$O$_5$ with respect to that of the ambient pressure form is a major advantage in terms of electrochemical applications.
4. Conclusions.
High pressure synthesis is a promising strategy to produce novel electrode materials, either polymorphs of well-known compounds or completely innovative materials. As an example, we have compared the electrode characteristics of the ambient pressure and the high-pressure polymorphs of V$_2$O$_5$. V$_2$O$_5$ (d = 3.32 g / cm$^3$) transforms under high pressure (40 kbar) into a polymorph, HP-V$_2$O$_5$, which possess a much denser structure (d = 3.80 g / cm$^3$). In spite of its higher density, HP-V$_2$O$_5$ also presents a layered structure, which facilitate the incorporation and mobility of cations in between the layers. Li // HP-V$_2$O$_5$ cells display a good cyclability and capacity retention with cycling of about 250 Ah/Kg. This behavior is comparable to that of the ambient pressure V$_2$O$_5$. Furthermore, the measured resistivites at room temperature (10000 Ωcm in AP and 400 Ωcm in HP) reveal that HP-V$_2$O$_5$ is indeed a better electronic conductor than AP-V$_2$O$_5$. These results demonstrate that materials obtained under high pressure can be suitable for electrochemical applications.

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