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# Mechanisms of enhanced lithium intercalation into thin film $V_2O_5$ in ionic liquids investigated by X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry

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## HIGHLIGHTS

- Atomic layer deposited $V_2O_5$ layer is used for lithium intercalation in ionic liquids.
- In $Pyr_{14}TFSI$, lithium intercalation has an average coulombic efficiency of 99%.
- Lithium insertion in presence of $Pyr_{14}TFSI$, exceeds the $V_2O_5$ theoretical capacity.
- The amount of lithium intercalated in $V_2O_5$ is similar in $Pyr_{14}TFSI$ and $Pyr_{13}FSI$.
- Formation of solid permeable interface (SPI) on the cathode surface is evidenced.

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## ABSTRACT

Room temperature ionic liquids (RTILs) attract much attention as a new type of environmentally benign electrolytes for Li-ion batteries due to their numerous interesting physicochemical properties. Here, in this paper, Li intercalation/deintercalation in presence of the *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ($PYR_{14}TFSI$) and *N*-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)imide ($PYR_{13}FSI$) containing 0.3 M LiTFSI, was evaluated in a thin 100 nm layer of $V_2O_5$ deposited on Al substrate by atomic layer deposition. Potentiodynamic tests performed in LiTFSI/$Pyr_{14}TFSI$ show a quasi-reversible Li intercalation during 10 cycles (between 2.4 and 5 V) with an average coulombic efficiency of 99%. The capacity, calculated from the 1st cycle, is found to be 182 mAh $g^{-1}$, about 19% (±2%) higher than the theoretical capacity reported for $V_2O_5$ (147 mAh $g^{-1}$). X-ray photoelectron spectroscopy analysis confirms that the intercalation of more than 1 mol of $Li^+$ per $V_2O_5$ is achieved as also the possible presence of a solid permeable interface (SPI) layer on the $V_2O_5$ surface. Likewise, the $Li^+$ in-depth distribution on the $V_2O_5$ layer after intercalation in RTILs measured by time-of-flight secondary ion mass spectrometry ion depth profiles, show small irreversible electrode modifications with the presence of lithium through the entire $V_2O_5$ layer with significant lithium trapping at the $V_2O_5$ layer/Al substrate interface.

## 1. Introduction

Due to particular physicochemical properties of room temperature ionic liquids (RTILs) (including high electrochemical stability, wide liquid phase temperature range, non-volatility, non-flammability and non-toxicity), they have attracted significant interest in different applications such as extraction of metals, electrodeposition of metals and metal oxides, catalysis and energy science and technology [1–11]. In the field of energy, ILs have been studied as new alternative electrolytes since a couple of years [1,2], most particularly in lithium-ion batteries [3], dye-sensitized solar cells [4], supercapacitors [5–7] or electrochemical actuators [8,9]. In the case of lithium-ion batteries, among the potential RTILs candidates,

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*N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($Pyr_{14}TFSI$) was found to have interesting properties such a reasonable room temperature ionic conductivity (>1 mS $cm^{-1}$) and a high electrochemical stability (around 5.5 V) [12]. Indeed, $Pyr_{14}TFSI$ was already tested as electrolyte for $Li^+$ intercalation on several materials such as Poly(3-methylthiophene) [13,14] and polypyrrole–$Fe_2O_3$ supercapacitors [15], composite silicon [16] and $FeSi_{2.7}$ [17] anodes, $Li_2FeSiO_4$ [18], $LiCoO_2$ [19], $0.5Li_2MnO_3$-$0.5Li(Mn_{0.375}Ni_{0.375}Co_{0.25})O_2$ [20] and $LiFePO_4$-based [21] cathodes or even in full cells such as $Li_4Ti_5O_{12}$//$LiCoO_2$ [22], $Li_4Ti_5O_{12}$//$LiFePO_4$ [23], Li//$LiMO_2$ (M = Mn, Ni, Co)-$Li_2MnO_3$ [24], Sn-C//$LiFe_{0.1}Co_{0.9}PO_4$ [25] and Au/$LiCoO_2$//$V_2O_5$ [26]. On the other hand, *N*-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)imide, ($Pyr_{13}FSI$) has a lower viscosity due to the reduced steric hindrance of the $(Pyr_{13})^+$ cation and, especially, the $(FSI)^-$ anion [27]. $Pyr_{13}FSI$ also exhibits a lower melting point, thus resulting in high conductivity values, also at low temperatures (*e.g.* 1 mS $cm^{-1}$ at −7 °C) [27]. Moreover, a reversible lithium intercalation/deintercalation into graphite was evidenced in the LiTFSI/$Pyr_{13}FSI$ electrolyte [12]. Nevertheless, $Pyr_{13}FSI$ display a lower electrochemical stability window than $Pyr_{14}TFSI$, around 5.4 V vs ~6 V, respectively [12], and also a much higher cost, which is related to the more difficult purification of the $FSI^-$ anion. According to our knowledge, only a few studies on the $Li^+$ intercalation into composite materials such as $Fe_2O_3$/C, CuO/$Cu_2O$/C, NiO/C anodes [28] and $LiCoO_2$ [29], $LiFePO_4$ [30] cathodes have been performed in presence of $Pyr_{13}FSI$.

At the same time, the development of miniaturized batteries (microbatteries) was sped up in recent years due to increase demands and applications in new fields such as microelectronic, medical or military industries. In microbatteries many studies have focused on a thin film technology for the development of deposition methods of thin film electrode materials [31]. One of the methods to prepare the thin film electrode material is the application of the atomic layer deposition (ALD) technique [32–37], which allows for a deposition of a conformal and uniform layer with well controlled thickness of different composite materials. The ALD has been used mostly for deposition of thin negative electrode materials for Li-ion batteries [38–43]. Indeed, there has been limited works reported on ALD positive electrode materials apart from $V_2O_5$ [44–54], $LiCoO_2$ [55], $FePO_4$ [56], and $LiFePO_4$ [57]. The ALD can be also used for a deposition of protective coatings on the surface of composite electrode materials to ensure the ionic diffusion and to compensates volumetric changes during charge/discharge process [58–63].

Amongst different transition metal oxides used as positive electrode materials, $V_2O_5$ can be considered as an interesting material, owing to its high theoretical capacity (437 mAh $g^{-1}$) [64] and low cost. In this perspective, many studies on the electrochemical performances of vanadium oxides in ionic liquid-based electrolytes have been undertaken [26,65–70]. Among these, only Strelcov et al. [71] have reported the use of $Pyr_{14}TFSI$ to study the lithium intercalation in $V_2O_5$ nanowires by *in situ* SEM. None of the abovementioned studies was performed on $Pyr_{13}FSI$.

In the present paper, we evaluate the efficiency of lithiation and delithiation as well as the formation of a surface passive layer onto thin (100 nm) $V_2O_5$ films deposited by ALD on an aluminium substrate, as cathode material in presence of $Pyr_{14}TFSI$ and $Pyr_{13}FSI$ ionic liquids comprising 0.3 M LiTFSI as electrolytes. The intention is to check the influence of the higher electrochemical stability of $Pyr_{14}TFSI$ and the lower viscosity and higher conductivity of $Pyr_{13}FSI$ in these processes. To the best of our knowledge, this is the first study using this type of RTIL electrolytes on ALD-processed $V_2O_5$ films. A detailed surface analysis was performed by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). The chemical bulk and surface modifications of $V_2O_5$ cycled in these ionic liquids is compared with those reported in the literature for $V_2O_5$ in presence of the conventional organic electrolytes.

## 2. Experimental

Thin $V_2O_5$ layers were deposited by atomic layer deposition (ALD) on aluminium substrates, by using a vertical type flow reactor (Picosun® SUNALE™ R-series). $OV(OCH(CH_3)_2)_3$ from STREM Chemicals Inc, purity > 98%, was used as precursor, ozone as oxidizing agent and nitrogen as carrier gas. The substrate was kept at 180 °C and the precursor was heated up to 150 °C. The deposition was performed using precursor pulse/purge/ozone pulse/purge times: 0.5 s/3 s/2 s/3 s. The deposition rate obtained was 0.27 Å/cycle. Before deposition, the aluminium substrates (Goodfellow – AL000770–99.999%: 1.5 × 1.5 × 0.3 cm) were polished with abrasive paper (SiC 800/2400), next with a suspension of $Al_2O_3$ (3, 1 and 0.3 μm) and then rinsed in ultra-pure Millipore® water (resistivity > 18 MΩ cm) and sonicated (15 min) in isopropanol. Finally, the Al substrates were dried under a flux of argon. The thickness of the ALD $V_2O_5$ layer deposited on a silicon wafer, using the aforementioned parameters, was determined through the measurement of a cross-section using a LEO 1530 VP Gemini field emission scanning electron microscope (FESEM) operated at an acceleration voltage of 10 keV. The deposited layer appeared to be homogeneous with a thickness of approximately 100 nm. The crystallinity of the as-deposited $V_2O_5$ film was confirmed by XRD (shown in Supplementary Information Fig. SI1), indicating the formation of orthorhombic $V_2O_5$ phase (JSPDS No. 41-1426) with no preferential growth direction.

The electrochemical assays were performed using a Bio-Logic (Science Instruments) modular 16 channels potentiostat/galvanostat. All electrochemical measurements were performed in the presence of the ILs $Pyr_{14}TFSI$ or $Pyr_{13}FSI$, both comprising 0.3 M LiTFSI, using a three-electrode electrochemical Kel-F cell (vol = 500 μL) set up using lithium foils (Aldrich) as reference and counter electrodes and $V_2O_5$ ALD thin films deposited on Al substrates ($V_2O_5$/Al) as working electrodes (surface area of 0.5 $cm^2$ delimited by a Viton O-ring). All potentials given in this paper are referred *versus* the Li/$Li^+$ reference electrode. The electrolytes were prepared using the 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($PYR_{14}TFSI$) (99.5%) and *N*-Propyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide ($PYR_{13}FSI$) (99.5%) RTILs and lithium bis-trifluoromethanesulfonimide *N*-methylpyrrolidine (LiTFSI) (99+%), which were purchased from Solvionic and used as received. The electrolytes preparation and all electrochemical experiments were done in an Ar-filled glove box (mBraun) with a controlled atmosphere ($H_2O$ < 0.1 ppm & $O_2$ < 0.1 ppm).

Cyclic voltammograms were recorded on $V_2O_5$ layers, in a potential range between 1 and 6 V, at a scan rate of 0.5 mV $s^{-1}$, and between 2.4 and 5 V, at 0.1 mV $s^{-1}$. Three separate tests were performed on these samples: one cycling the sample up to 10 cycles in 0.3 M LiTFSI/$Pyr_{14}TFSI$ (with a cut-off potential of 5 V for the deintercalated sample) and two others performing linear sweep voltammetry between 3.5 V (OCP) and 2.4 V in 0.3 M LiTFSI/$Pyr_{14}TFSI$ and 0.3 M LiTFSI/$Pyr_{13}FSI$ (with a cut-off potential of 2.4 V for the intercalated samples). After the electrochemical experiments, the $V_2O_5$ samples were rinsed with anhydrous acetonitrile (99.8% purity, Aldrich), dried in Ar flow and directly transferred to the ultra-high vacuum XPS or ToF-SIMS analysis chamber without exposure to air.

An XPS Thermo Electron Escalab 250 spectrometer with a UHV preparation chamber directly connected to the glove box was used for surface characterization. An Al Kα monochromatized radiation