HYDROTHERMAL SYNTHESIS OF NANO BILAYERED $\text{V}_2\text{O}_5$
AND ELECTROCHEMICAL BEHAVIOR IN NON–AQUEOUS ELECTROLYTES LiPF$_6$ AND NaClO$_4$

Huynh Le Thanh Nguyen$^1$, *, Nguyen Van Hoang$^2$, Nguyen Thi Ngoc Dieu$^1$, Huynh Bang Vy$^1$, Le My Loan Phung$^{1,2}$, Tran Van Man$^2$

$^1$Applied Physical Chemistry Laboratory, Faculty of Chemistry, University of Science–VNUHCM, 227 Nguyen Van Cu, District 5, Ho Chi Minh City, Vietnam
$^2$Department of Physical Chemistry, Faculty of Chemistry, University of Science–VNUHCM 227 Nguyen Van Cu, Ward 4, District 5, Ho Chi Minh City, Vietnam

*Email: hltnguyen@hcmus.edu.vn

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ABSTRACT

This work aimed to prepare bilayered $\text{V}_2\text{O}_5$ by hydrothermal route from vanadium (III) chloride ($\text{VCl}_3$). According to XRD results, bilayered $\text{V}_2\text{O}_5$ showed a large interlayer spacing around 11.3 Å. The electrochemical properties of bilayered $\text{V}_2\text{O}_5$ were carried out by cyclic voltammetry and charge–discharge testing in non–aqueous electrolytes LiPF$_6$ and NaClO$_4$. The curves charge–discharge showed that mechanism of insertion/extraction of Li$^+$ ions and Na$^+$ ions were occurred on a solution solid without the phase transition. Moreover, specific capacity for lithium and sodium intercalation of bilayered $\text{V}_2\text{O}_5$ were found out 250 mAh/g and 200 mAh/g, respectively. The kinetic of lithium’s and sodium’s insertion was evaluated by the electrochemical impedance spectroscopy (EIS). The EIS results exhibited a stabilization of charge transfer in both case and a slow kinetic of sodium’s diffusion compared to lithium’s case due to the large ionic radius of sodium.

Keywords: electrochemical impedance spectroscopy, kinetics, lithium’s intercalation, sodium’s intercalation, bilayered $\text{V}_2\text{O}_5$.

1. INTRODUCTION

In 21$^{\text{th}}$ century, rechargeable batteries are main key of modern technology in many applications from portable devices (smartphone, laptop…) to large–scale (hydride electric vehicle–HEV, smart grid system…) [1–3]. Among the rechargeable batteries, Li–ion battery (LIB) is outstanding member due to the highest gravimetric as well as volumetric capacity; and Sodium–ion batteries (SIBs) can have contribution to alternating LIBs in large–scale application. Li–ion and Na–ion batteries have the same configuration with an insertion/extraction reversible of Li$^+$ ions and Na$^+$ ions into electrode positive and negative during charge–discharge process [4, 5].
Bilayered V$_2$O$_5$ is a promising cathode material for both Li–ion and Na–ion batteries because of a large interlayer spacing around 10 Å [6, 7]. In this work, we investigate the insertion electrochemical of Li$^+$ ion and Na$^+$ ion into bilayered V$_2$O$_5$ in non–aqueous electrolyte. Moreover, a comparison of kinetics of lithium–sodium intercalation into nano crystalline V$_2$O$_5$ bilayered was carried out. The electrochemical impedance spectroscopy results exhibited the slow kinetics of sodium intercalation compared to lithium intercalation due to the large ionic radius of sodium.

2. MATERIALS AND METHODS

Bilayered V$_2$O$_5$ were prepared by a hydrothermal route. A mixture of 1 mmol of VCl$_3$ (Sigma–Aldrich, 97 %), 5 mL pyridine (Sigma–Aldrich) and 10 mL deionized water was stirred under vigorous at room temperature. After that, the precursor solution was heated at 180 °C in a teflon–lined autoclave for 12 hours. The precipitate was cooled to room temperature naturally, collected, and washed with deionized water and ethanol several times. The final products were obtained after drying at 120 °C in a vacuum oven overnight. Structures of these samples were identified by powder X–ray diffraction, using a X’Pert PRO MPD PANalytical diffractometer (at Center for Innovative Materials and Architectures, Ho Chi Minh City) with CoK$\alpha$ radiation ($\lambda = 1.789$ Å), 0.02° and 20 second pars step counting time. The diffraction pattern was collected for 2$\theta$ between 10° to 70°. The morphology and the distribution of grain size were determined by using a FE–SEM S4800 (Hitachi, Japan) at Institute of Chemical Technology–VAST.

The electrochemical properties were measured in a Swagelok–type cell. The positive electrode was composed on material active (80 wt%), acetylene black (7.5 wt%), graphite (7.5 wt%) and teflon (5 wt%). The mixture was pressed directly on a stainless–steel grid under a pressure of 5 ton/cm$^2$. Negative electrode was lithium or sodium metal and 1 M LiPF$_6$/ethylene carbonate:dimethyl carbonate or 1 M NaClO$_4$/propylene carbonate (2 % fluoroethylene carbonate) were used as electrolyte, respectively. Cells were assembled in a glove box under argon to avoid oxygen and water. The kinetic of insertion–extraction of lithium or sodium into bilayered V$_2$O$_5$ were investigated by using electrochemical impedance spectroscopy. Impedance measurements were performed in the frequency range from 10$^6$ Hz to 5×10$^{-3}$ Hz. The excitation signal was 10 mV peak to peak. Electrochemical studies were carried out by using VMP3 apparatus (BioLogic–France). All electrochemical characterizations were implemented at Faculty of Chemistry, University of Science–VNUHCM.

3. RESULTS AND DISCUSSION

3.1. Structure and morphology

The bilayered V$_2$O$_5$, called V$_2$O$_5.n$H$_2$O xerogel, is a stack of long ribbon like slabs which are made up of octahedral [VO$_6$] stacked along c–axis, as shown in Figure 1a with a distance inter–layer of 11.5 Å [8–10]. The XRD pattern of bilayered V$_2$O$_5$ (Figure 1b) showed the typical (00l) reflection peaks, which are consistent with those of the layered structure of V$_2$O$_5.n$H$_2$O (JCPDF: 40–1296). According to XRD pattern, the distance interlayer was determined to 11.7 Å.

Due to the hydrothermal reaction, the peaks in XRD pattern had quite large. It is considered that the sample was crystallized in small particle sizes. According to the Debye–Scherrer equation (1), the average size of particles was calculated from the full width of half maximum (FWHM) of diffraction peaks:
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\[ d_{hkl} = \frac{k\lambda}{\beta \cos \theta} \]  

(1)

where \( d_{hkl} \) is the average size, \( k \) is the constant depending on the crystallite shape (0.9), \( \lambda \) is the wavelength of CoK\(\alpha \) X–ray radiation (1.789 Å), \( \beta \) is the FWHM of the most intense peak, and \( \theta \) is the diffraction angle. The size reached around 20 nm. The nanosize of particles will suggest a fast kinetic of intercalation of lithium and sodium ion due to shortening the pathway of diffusion.

As can be seen in Figure 2, the sample bilayered V$_2$O$_5$ had a homogenous grain distribution, and the particle size fell into the micrometric dimension scale. The particle size was around 1 μm.

![Figure 1. Structure of bilayered V$_2$O$_5$ and XRD pattern of sample.](image1)

![Figure 2. SEM images of bilayered V$_2$O$_5$.](image2)

3.2. Electrochemical properties

During charge–discharge process, the insertion/extraction of Li$^+$ ions and Na$^+$ ions into bilayered V$_2$O$_5$ occur following electrochemical reaction:

\[ V_2O_5 + xA^+ + xe^- \leftrightarrow A_xV_2O_5 \]

where \( A^+ \) may represent a monovalent cation (Li$^+$ and Na$^+$). Here, the forward reaction is called intercalation (insertion, discharge), while the backward reaction is termed deintercalation (extraction, charge). Intercalation and deintercalation proceed reversibly in opposite directions.

Figure 3a showed the typical charge–discharge curves of bilayered V$_2$O$_5$ in non–aqueous 1 M LiPF$_6$/EC:DMC (1:1) solution at window potential 1.5–4.2 V (vs. Li$^+$/Li). All the charge–discharge curves showed a totally reversible intercalation of Li$^+$ ions. In the 1$^{st}$ cycle, the host
could insert 1.5 Li$^+$ ions, corresponding to a maximum specific capacity of 230 mAh/g. Moreover, the curves represent a low polarization as well as a simply form that indicates an uncomplicated insertion of Li$^+$ ions with a mechanism of solution solid. The cycling performance was presented in Figure 3b; after fifteen cycles, a specific capacity reduced to 150 mAh/g.

Figure 3. (a) Typical charge–discharge curves and (b) cycling performance of bilayered V$_2$O$_5$ in 1 M LiPF$_6$/EC:DMC (1:1).

Figure 4a showed the typical charge–discharge curves of bilayered V$_2$O$_5$ in non–aqueous 1 M NaClO$_4$/PC (2 % FEC) solution at window potential 1–4 V (vs. Na$^+$/Na). In 1$^{\text{st}}$ cycle, an irreversible insertion of Na$^+$ ions were observed, bilayered V$_2$O$_5$ could insert 1.35 Na$^+$ ions in the 1$^{\text{st}}$ reduction but only 0.9 Na$^+$ ions could extract in oxidation. This result exhibited a relation structural of bilayered V$_2$O$_5$ and α–V$_2$O$_5$. In α–V$_2$O$_5$ case, the sodium's insertion accompanied with an electrochemically formed phase α'–NaV$_2$O$_5$ [11]. In 2$^{\text{nd}}$ cycle, we observe a reversible insertion of sodium ions. All the curves showed a large polarization that suggested a strong interaction of Na$^+$ ions and bilayered structure. The cycling performance was presented in Figure 4b; after thirty cycles, a specific capacity reduced to 100 mAh/g.

Figure 4. (a) Typical charge–discharge curves and (b) cycling performance of bilayered V$_2$O$_5$ in NaClO$_4$ 1 M/PC (2 % FEC).

3.3. Kinetic of lithium’s and sodium’s intercalation

Kinetics of alkaline ion’s transport into bilayered V$_2$O$_5$ was determined by electrochemical impedance spectroscopy method. The impedance measurements were performed in the frequency range 10$^2$ Hz to 5×10$^{-3}$ Hz at a various content of alkaline ion. The diffusion
coefficients of alkaline ion D were calculated from region Warburg by following equation (2) [12]:

$$D_{Li/Na} = \left( \frac{V_M}{\sqrt{2FS}} \times \frac{dE}{dx} \times \frac{1}{A_{m}} \right)^2$$

(2)

where, VM is the molar volume of host (V_m = 54.5 cm³/mol); S is the active surface of electrode (0.785 cm²); |dE/dx| is the slope at fixed x and determined by curve C/60, A_m is the slope of relation between Z_real and ω⁻¹/₂ in the Warburg impedance.

For lithium’s intercalation, the diagram impedance presented three regions. A semi–circle in the high–medium frequency corresponded to the charge transfer with a characteristic frequency f₀ = 63 Hz. An unchanged characteristic frequency proposed a stabilization of “quasi–resistance of charge transfer”. The low frequency region, a straight line 45° (1–0.1 Hz) from the real axis demonstrated the Warburg impedance and at lower frequencies (f < 10⁻³ Hz) the phase angle was increasing which belonged to the finite diffusion process (Figure 5). The semi–infinite diffusion allowed to calculate the lithium diffusion coefficients: D_{Li} = 1.3×10⁻⁹ cm²/s for x_{Li} = 0.1 and D_{Li} = 8.9×10⁻⁹ cm²/s for x_{Li} = 0.4. These values were coherent with the lithium diffusion coefficients in α–V₂O₅ and bronzes MₓV₂O₅.

In case of sodium’s intercalation, the diagram impedance exhibited the same model (Figure 6). However, the “quasi–resistance of charge transfer” in sodium’s case was larger than lithium’s case, and the Warburg region in sodium’s case was found at lower frequencies (0.4–0.02 Hz). It could be explained by the passivation and evolution of sodium’s surface during the discharge process and a larger ionic radius of sodium ion. The sodium diffusion coefficients were found D_{Na} = 9.5×10⁻¹¹ cm²/s for x_{Na} = 0.1 and D_{Na} = 1.2×10⁻¹¹ cm²/s for x_{Na} = 0.4.
4. CONCLUSIONS

In summary, we had synthetized nano–crystalline bilayered $V_2O_5$ by hydrothermal rout from a precursor of $VCl_3$. The XRD pattern of bilayered $V_2O_5$ showed the typical (00l) with an interlayer spacing of 11.7 Å. Bilayered $V_2O_5$ could insert reversibly 1.5 ion Li$^+$ (~220 mAh/g); while a stability of sodium’s intercalation occurred at 0.8 ion, corresponding to a specific capacity of 120 mAh/g. The sodium diffusion coefficients were found around $10^{-11}$ cm$^2$/s, This value is lower 100 times than the lithium diffusion coefficients (~$10^{-9}$ cm$^2$/s) due to a larger ionic radius of sodium ion.

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