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Facile hydrothermal synthesis of economically viable VO$_2$(M1) counter electrode for dye sensitized solar cells

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Abstract

In this study, we focus at reducing the fabrication cost of dye sensitized solar cells (DSSCs). Sphere-like VO$_2$(M1) polymorph was synthesized by single step facile hydrothermal approach using citric acid as the reducing agent. Phase purity, charge state and surface morphology of the synthesized product was confirmed by X-ray diffraction, X-ray photoelectron spectroscopy and scanning electron microscopy respectively. The electrochemical impedance and cyclic voltammograms of VO$_2$ films indicated a good electrocatalytic activity towards redox reaction of the I$^-$/I$_3^-$ shuttle. Owing to the low cost, low-temperature processing and good catalytic activity, in this work we propose to use VO$_2$ as a counter electrode to substitute the expensive platinum.
electrode in DSSCs. By means of VO$_2$ based DSSCs we achieved a **fivefold** reduction in the cost to energy conversion efficiency ratio. It is expected that with further optimization, VO$_2$ can be exploited as a good candidate for counter electrode in DSSC technology.

**Keywords:** A. layered compounds; B. oxides; C. chemical synthesis; D. impedance spectroscopy; E. catalytic properties

1. Introduction

Draining of natural resources is bringing a global energy crisis, ever closer yet solutions are possible such as a shift to renewable energy sources. Solar energy is the largest natural energy resource which can be explored and utilized much more generously [1]. Dye sensitized solar cells (DSSCs) technology which convert light into electricity has gained a lot of attention due to their key features such as low fabrication cost, environmental compatibility, price-to-performance ratio, ability to work at wider angles and in low light [2,3]. A typical DSSC consists of a metal oxide as an active electrode, a light harvesting dye, a redox electrolyte and a counter electrode (CE). The chief concern in the commercialization of DSSCs is cutting down the manufacturing cost further, while keeping up decent efficiencies and lifetime. The principle production cost of DSSCs depends on the materials cost and fabrication process. The CE is a vital component which transfers the electrons from the external circuit to the internal electrolyte and as a whole, reduces the tri-iodide ions to iodine ions, which eventually realizes the operation of DSSCs.

Conventionally, platinum (Pt) on fluorine doped tin oxide (FTO) coated glass is used as a CE. Platinum is chosen because of its high electrocatalytic activity, conductivity and chemical affinity to reduce tri-iodide [4]. However, the major concern here is, Pt being expensive and having limited natural availability which primarily restricts the production of DSSCs at large
scale. Hence, there is a pressing need for the identification of economically viable CE materials, exhibiting high photovoltaic performance and stability. Thus many researchers have been focusing on alternative materials to Pt with similar characteristics. In the recent years, the number of reports concerning the alternative CEs has increased significantly. For the current state of art of Pt-free CEs, the reader may refer to review papers elsewhere [4-9]. Apart from high catalytic activity and high electrical conductivity, the prime characteristics for choosing an alternative material for CEs are abundance in nature, environmentally friendly, stability and economic viability for large scale production.

Transitional metal oxides (TMOs) are of particular interest for this type of application, because of their excellent atmospheric stability, low cost, abundance in nature, good catalytic and electrical conductivities. Despite these advantages less effort has been devoted to exploit TMOs as CEs until this decade. Recently TMOs such as WO₂, WO₃, ZrO₂, TiO₂, Cr₂O₃, MoO₂, Nb₂O₅, NiO, V₂O₅ and V₂O₃ are reported as CEs in electrolyte based DSSCs and V₂O₅ composite in solid state DSSCs [10-15]. In TMOs family, vanadium based oxides are receiving huge interest in the field of energy storage technologies such as batteries and super capacitors, because of their diverse chemical motifs, layered structure, high energy capacity and moderate work functions [16,17]. From the economical point of view, the raw materials cost of vanadium based oxides estimated from Sigma-Aldrich catalogue show 30 times less than that of Pt of the same purity level. The VO₂ compound exhibits several stable polymorphs such as VO₂(M1), VO₂(R), VO₂(B), VO₂(A), VO₂(D), VO₂(BCC) and VO₂(N) [18]. In particular the VO₂(M1) polymorph has attracted tremendous attention for electronic, thermochromic and optical applications such as smart windows and electrical switches [19-21]. In this work, we propose and demonstrate VO₂(M1) to be used as a CE in DSSCs.
To the best of our knowledge, it is the first time that VO$_2$(M1) has been explored as a CE in DSSC technology. We report here a simple hydrothermal route to synthesize the pure VO$_2$(M1) polymorph. We have carried out detailed characterization of synthesized product and investigated the photovoltaic performance for VO$_2$(M1) CEs in DSSCs.

2. Experimental

2.1. Materials synthesis

The synthesis of VO$_2$(M1) via a hydrothermal process is as follows: Initially V$_2$O$_5$ (Aldrich) was dissolved in 35 mL of deionized water. After stirring for 15 min using a magnetic stirrer, 1.5 molar ratio to V$_2$O$_5$ of citric acid monohydrate (C$_6$H$_8$O$_7$·H$_2$O; Merck) was added into the solution and stirring was prolonged for another 15 min. The resultant yellowish green aqueous solution was transferred into the Teflon lined stainless steel autoclave. The sealed steel autoclave was placed in a high temperature oven at 250 °C. After 24 hrs, the autoclave was slowly cooled to room temperature naturally. The as obtained bluish-black powder samples were filtered and washed several times with distilled water and ethanol to remove unreacted chemical species and dried in air at 80 °C for 6 hrs and then used for further characterizations.

2.2. Fabrication of dye sensitized photoelectrodes

The photoelectrodes (PEs) are prepared as follows: first FTO coated glass substrates (Pilkington TEC glass™, sheet resistance: 11.7 Ω/sq, 2.2 mm in thickness, TEC-12) were cut into small pieces (2 × 2 cm). The substrates were first cleaned thoroughly with Teknon microcleanse detergent solution, ultrasonicated in deionised water followed by acetone and isopropanol for 15 min at each step, and then dried in flowing nitrogen to further remove any solvent traces. Afterwards the substrates were transferred into a 40 mM TiCl$_4$ solution container.
and heated for 1 hour at 80 °C to form a compact layer of TiO₂. Later the substrates were rinsed thoroughly with deionised water followed by dry in flowing nitrogen. Commercial nanocrystalline TiO₂ paste (DSL 18NR-T, Dyesol as the transparent layer) was screen printed on the compact layered FTO substrates, afterward TiO₂ scattered paste (DSL 18NRAO, Dyesol as the scattering layer) was deposited by screen printing. The active screen printed areas were approximately 1 cm². The TiO₂ coated films were then successively sintered in ambient on a hotplate in a series of steps such as at 325 °C for 10 min, at 375 °C for 5 min, at 450 °C for 15 min and at 500 °C for 15 min, and finally were cooled down naturally to room temperature. Later these electrodes were further treated with 40 mM TiCl₄ for 30 min at 80 °C and consequently sintered at 450 °C for 30 min and then allowed for cooling. As soon as these photoelectrodes reach 80 °C, these films were subsequently immersed in N719 (Dye-sol) solution and kept in an air-tight glass container at room temperature under dark and dry conditions for 20 hours. Dye sensitized photoanodes were rinsed with iso-propanol followed by drying with nitrogen flow at room temperature.

2.3. Fabrication of counter electrodes

First a small hole was drilled on FTO coated glass substrates using a sand blasting unit, with a smooth finish given by ending the drilling with a portable glass hole drilling tool. These drilled FTO substrates were subjected to the same cleaning and drying processes as aforementioned. A thick viscous paste of VO₂ was prepared by mixing 4:1 ratio of hydrothermally synthesized VO₂ powder and ethyl cellulose and by adding few drops of α-terpineol. This paste was deposited on FTO coated glass by screen printing and later sintered at 450 °C for 30 mins under inert atmosphere at a heating rate of 5 °C/min to remove the organic
binders. Reference electrodes were prepared by depositing Pt on FTO glass substrates by means of sputtering.

2.4. Photovoltaic cell assembly

The N719 dye sensitized TiO$_2$ PEs and CEs were assembled into a sandwich configuration with a spacer between the two electrodes. Subsequently the liquid electrolyte (composed of 0.05 M Iodine, 0.1 M lithium iodine, 0.6 M 1-butyl-3-methylimidazolium iodide and 0.5 M 4-tertbutyl pyridine in a mixture of acetonitrile and valeronitrile) was injected via drilled hole into the space between these electrodes. Finally the holes were sealed with a polymer film of 25 μm thickness (Metlonix 1170, Dupont surlyn) and glass cover. The schematic of the final assembled device is shown in Fig. 1.

2.5. Material and device characterizations

The phase purity and crystallographic structure of VO$_2$ powder was determined using automated PANalytical X’ Pert Diffractometer, Netherlands (using Ni filtered Cu K$_{α1}$ radiation, $λ=1.5406$ Å). To further access information about the degree of oxidation of vanadium and thereby the composition and the electronic structure of VO$_2$, we carried out X-ray photoelectron spectroscopy (XPS) measurements on powder sample at room temperature. The XPS spectrum was acquired using a Kratos Analytical AMICUS XPS instrument and a Mg K$_{α1}$ X-ray source operated at 150 W (10 kV, 15 mA). The surface morphology of VO$_2$ powder sample and the screen printed VO$_2$ CE was investigated by field emission scanning electron microscopy (FESEM) (XL30 ESEM). The photocurrent density and photovoltage characteristics of DSSCs were measured by computer controlled digital source meter (Keithley 2400) under AM 1.5 one sun (100 mWcm$^{-2}$) illumination using a solar simulator (92250 A, Newport, USA). An
electrochemical work station system (Autolab potentiostat equipped with FRA2 module) was employed to measure the internal resistances of the assembled final cells. Cyclic voltammetry measurements over the VO$_2$ and Pt CEs were performed at room temperature using a μAUTOLAB Type III Potentiostat set-up which was driven by the electrochemical software GPES.

3. Results and discussion

3.1. Structural and morphological characterization

In order to know the phase formation and the crystallinity of the as synthesized powder samples, X-ray diffraction (XRD) study was carried out at room temperature. Fig. 2a shows the XRD patterns of the as-prepared VO$_2$ powder and as well as VO$_2$ CE. For the same XRD acquisition time, the stronger diffraction peaks observed in the case of CE indicates that thermal annealing improved the crystallinity. All the diffraction peaks exhibited in the XRD patterns can be readily assigned to the monoclinic phase of VO$_2$(M1) (JCPDS card no. 01-082-0661). The room temperature crystal structure details are determined from Le bail fits using the FullProf program [22]. In the case of powder and thin film samples, the lattice parameters are extracted as a=5.753(3) Å, b=4.532(3) Å, c=5.364(1) Å, β=122.40(2)$^\circ$ and a=5.7503(4) Å, b=4.5246(3) Å, c=5.3812(4) Å, β=122.59(2)$^\circ$ respectively. No diffraction peaks corresponding to any other vanadium oxide phases are detected either in the powder sample or from the screen printed CE.

To further access information about the degree of oxidation of vanadium and thereby the composition and the electronic structure of VO$_2$, we carried out XPS measurements on powder sample at room temperature. The XPS spectrum shown in Fig. 2b revealed binding energy levels that correspond to vanadium and oxygen (which are the chemical elements in VO$_2$) and atmospheric carbon. No other peaks of impurity elements are noticed. For our XPS analysis, the
binding energy (BE) of the adventitious carbon C 1s = 284.6 eV is taken as an energy calibration reference. Fig. 2b inset shows the valence band (VB) region and core level spectra for vanadium and oxygen elements in VO$_2$. The high resolution XPS VB region consists of V 3d and O 2p levels in the energy ranges between 0-2 and 3-9 eV, respectively as shown in the inset of Fig. 2b. The zero spectral weight at the Fermi level supports the nonmetallic behavior of VO$_2$(M1) at room temperature. From core level XPS spectra, we noticed the BE levels of V 2p$_{3/2}$ and O 1s peaks which are centered at 516.41 eV and 529.84 eV, respectively (see Fig. 2b). These are characteristic energy levels of the V$^{4+}$ oxidation state and in good agreement with most of the reported values. Besides the V$^{4+}$ 2p$_{3/2}$ core level one more minor contribution is visible around 517.15 eV. From the literature, it is clear that this BE level corresponds to V$^{5+}$ 2p$_{3/2}$ and this could be due to surface oxidation of the VO$_2$ powder samples [23]. Similarly a second component is visible in the O 1s signal at 531.2 eV. It can be attributed to surface contamination by atmospheric carbon. The O 1s BE reported for C=O is within 530.7–531 eV and the extra shoulder to the O1s peak (531.2 eV) thus falls into the region of C=O O 1s. In addition, this is also consistent with the components in the C 1s spectrum where we found a shoulder at 287.6 eV, which is a 3.0 eV higher binding energy than the C–C bond (284.6 eV) [24]. Due to a wide spread in the XPS BE values reported for vanadium oxides, Mendialdua et al. proposed that difference in binding energies between the O 1s core level and the V 2p$_{3/2}$ core level ($\Delta E =$ BE(O1s)–BE(V 2p$_{3/2}$)) is a better determination of vanadium oxidation degree [25]. According to this, $\Delta E$ is between 17.65-17.90 eV, 16.33-18.4 eV, 14.2-14.85 eV, 13.45-14.5 eV and 12.6-12.9 eV for V$^0$, V$^{2+}$, V$^{3+}$, V$^{4+}$ and V$^{5+}$ oxidation degrees, respectively. In our case, the BE difference ($\Delta E$) between the vanadium core level (V 2p$_{3/2}$) and the oxygen core level (O 2p) is 13.65 eV.
This is in agreement with +4 oxidation degree of V and confirms the chemical composition as VO$_2$.

For further studying the structure feature, the morphology and microstructure of VO$_2$ powder and the screen printed VO$_2$ CE was observed using FESEM. Fig. 3 displays the SEM images of both powder and thin film CE. The low magnification image as seen in Fig. 3a, clearly depicts evidence of large-scale uniformity of the hydrothermally synthesized VO$_2$. The zoom view of the marked area in this image shows the specimen is mainly composed of a mass of spheres and a small ‘fluffy’ structure. Further close inspection reveals these spherical structures to resemble that of woolen balls with diameters ranging from hundreds of nanometers to about 7 micron. The morphology of an annealed VO$_2$ film is shown in Fig. 3c and Fig. 3d, which appears to be dense and uniform without cracks. Fig. 3d shows the high magnification image of the marked area in Fig. 3c. In comparison to the original appearance of as synthesized powder, the screen printed film has an obvious change in the morphology, which is reflected by the presence of fewer spherical structures, as some of these micro spheres are crushed into smaller particles during the grinding process while making the viscous paste for screen printing.

3.2. Photovoltaic performance

Fig. 4 displays the photocurrent density - photovoltage (J-V) curves of the device characteristics of DSSCs with VO$_2$ and sputtered Pt CEs. These results were obtained using the sandwich structure shown in Fig. 1. The photovoltaic parameters of these devices including series and shunt resistances (R$_s$ and R$_{sh}$) are summarized in the Table 1. The DSSC with VO$_2$ CE yielded an overall photoconversion cell efficiency ($\eta$) of 1.25%, short-circuit photocurrent density ($J_{sc}$) = 4.67 mAcms$^{-2}$, open-circuit photovoltage ($V_{oc}$) = 0.61 V, fill factor (FF) = 43.72%. The results of DSSCs with conventional Pt electrodes produced of 7.08% ($J_{sc}$=14.90 mAcms$^{-2}$,
$V_{oc} = 0.64\, \text{V}, \, \text{FF} = 73.74\%$). The $V_{oc}$ of both the samples are similar, as the photoanode and the dye are the same, whereas the lower values of $J_{sc}$ and FF in VO$_2$ CE indicating towards less utilization efficiency of photogenerated electrons than that of Pt CE [26]. $R_s$ and $R_{sh}$ values are extracted from the inverse slopes of the light J-V curves. Both cells exhibit a similar $R_{sh}$ of about 2.8 KΩcm$^{-2}$, whereas $R_s$ values of 27 and 5 Ωcm$^{-2}$ for VO$_2$ and Pt were respectively. The inferior efficiency of VO$_2$ based cells to that of Pt based DSSCs is mainly linked to low FF. It is known that the FF is influenced by $R_s$ and $R_{sh}$ of the solar cell. The FF reflects the extent of electrical and electrochemical losses during DSSC operation. As both cells exhibit similar $R_{sh}$ value, it implies that further understanding of $R_s$ is crucial. This will help to decrease $R_s$ value to eventually increase the corresponding FF. To ensure reproducibility of the DSSCs, six cells of VO$_2$ DSSCs were fabricated and tested.

3.3. Electrochemical characterization

In order to better understand the electrocatalytic performance of proposed CE towards the reduction of $I_3^-$, electrochemical impedance spectroscopy (EIS) measurements were conducted on full cells fabricated with CEs of VO$_2$ and for reference Pt CEs was used. The impedance spectra were collected under dark conditions at a bias of 0.8 V in the frequency range 0.1 Hz to 1 MHz. The obtained Nyquist plots of Pt and VO$_2$ full cells are displayed in Fig. 5a and Fig. 5b, respectively. The EIS spectra exhibited two semicircles, which describe the different impedance contributions of DSSC. In case of Pt the semicircles are well defined whereas in VO$_2$ (M1), the semicircles are convoluted. In inset figure the encircled portion of Fig. 5b data is plotted in close up for better visibility. The first semicircle in the high frequency region (on the extreme left) describes the charge transfer resistance at the CE/electrolyte interface ($R_{ct}$). The $R_{ct}$ is determined by the diameter of the high frequency semi-circle in the Nyquist plots and its
magnitude is our main focus since the CE used for DSSCs is responsible for this. It is known that the total internal series resistance of a DSSC is the sum of sheet resistance of the transparent conducting oxide substrates, \( R_{ct} \) and the diffusion resistance of I\(_3^-\) ions in the electrolyte. In this work, all the devices are assembled using the same photoanode and electrolyte except the counter electrode. This suggests the different internal series resistance values obtained can be attributed to the Ohmic losses in the electrolyte and between the electrolyte and the counter electrode layer. From Nyquist plots, it is evident that the magnitude of \( R_{ct} \) of a VO\(_2\) based DSSC is relatively higher than that of conventional Pt based one. This indicates that the total internal impedance of the VO\(_2\) DSSC is higher which has a direct influence on the electron transport mechanism in DSSCs. As an effect, the cell performance of the VO\(_2\) based DSSCs is lower compared to conventional Pt, which is in consonance with J-V curves.

To further evaluate the catalytic activity of the proposed CE towards the iodine/tri-iodide (I\(^-/I_3^-\)) redox couple is studied by cyclic voltammetry (CV). The CV spectra were recorded at a scan rate of 50 mV/s in a three electrode system in a freshly prepared anhydrous acetonitrile solution containing 0.1 M LiClO\(_4\), 10 mM LiI and 1 mM I\(_2\), which was purged with nitrogen prior to each measurement. The three electrode system comprised of Ag/AgCl as the reference electrode, Pt wire as the counter electrode and sputtered Pt or VO\(_2\) screen printed on FTO glass as the working electrode. Cyclic voltammograms of I\(^-/I_3^-\) redox mediator on both Pt and VO\(_2\) CEs are shown in Fig. 6. The Pt CE shows two pairs of distinctive redox peaks at \( E_{ox1} = 524 \) mV, \( E_{red1} = 91 \) mV and \( E_{ox2} = 997 \) mV, \( E_{red2} = 665 \) mV which demonstrates its good catalytic activity.

The lower potential redox pair is attributed to the oxidation and reduction of I\(^-/I_3^-\) whereas the higher potential pair is assigned to the oxidation and reduction of I\(_2/I_3^-\). The VO\(_2\) CE has shown one broad oxidation peak at lower potential \( E_{ox1} = 161 \) mV and a reduction peak whose
value is not well defined. Peak to peak separation (EPP) is an important parameter, which qualifies the catalytic activity of CEs. The EPP value for the Pt electrode was found to be 524 mV but due to the broad reduction of VO\(_2\) CE the EPP value could not be estimated. The increase in interfacial charge transfer resistance in the VO\(_2\) based DSSC obtained from EIS spectra lowers the FF of the device, which is the main reason for low photovoltaic efficiency and is further supported by its corresponding CV performance. Furthermore, enhancement of electrical conductivity of VO\(_2\) can be achieved by tuning the electronic properties by means of doping with elements such as Mo and W. Along with doping, the other possibility to promote the electrical conductivity is by preparing VO\(_2\)/carbon composites. The number of reaction sites for catalytic activity can be upgraded by tuning the morphology of the synthesized product. It is believed combining both of the aforementioned steps certainly will enhance the utilization efficiency as a result of enhancement of the charge transfer ability and the number of reaction sites [27].

4. Conclusion

In summary, our report shines light on the potential of an inexpensive, abundant and easily scalable material as a CE in DSSC technology to replace the popular choice Pt which prohibits the large scale production because of its cost. The VO\(_2\)(M1) polymorph has been investigated as an alternative CE material in DSSCs. We have synthesized VO\(_2\) using a single step, simple hydrothermal synthesis. The phase confirmation of the synthesized product was done by XRD and XPS. The SEM micrographs evidence that the VO\(_2\) powder is composed of uniformly distributed spherical particulates. The CV and EIS studies demonstrate the electrocatalytic activity of the screen printed VO\(_2\) CEs. The photoconversion efficiency of the best cell achieved was 1.25%. These results revealed that the \(V_{oc}\) and \(R_s\) of the DSSC obtained
using VO₂ as the CE are significant in the first attempt of study though inferior to that of the DSSCs made of Pt CEs. Our future investigations will be focused on enhancing the efficiency, the stability and the long term operation of DSSCs made with VO₂ CEs. Though the obtained efficiencies are still below that of Pt, these primary results are encouraging and provide a scope to the search for abundant and low cost, environmentally friendly materials as an effective alternate for DSSCs.

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References


Table 1. Photovoltaic parameters of DSSCs using VO$_2$ and Pt CEs.

<table>
<thead>
<tr>
<th>Counter Electrode</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (Ω cm$^{-2}$)</th>
<th>$R_{sh}$ (KΩ cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO$_2$</td>
<td>0.61</td>
<td>4.67</td>
<td>43.72</td>
<td>1.25</td>
<td>27</td>
<td>2.84</td>
</tr>
<tr>
<td>Pt</td>
<td>0.64</td>
<td>14.90</td>
<td>73.74</td>
<td>7.08</td>
<td>5</td>
<td>2.85</td>
</tr>
</tbody>
</table>
Figure captions page

**Fig. 1.** Schematic representation of the assembled liquid based DSSC. It is comprised of transparent conducting oxide (FTO) on glass, a nanoparticle photoelectrode (such as TiO$_2$) sensitized with N719 dye, hole-conducting iodine based liquid electrolyte and platinum or VO$_2$ deposited on FTO coated glass back contact.

**Fig. 2.** Powder XRD patterns of VO$_2$ powder and screen printed VO$_2$ CE; star symbol represents the Bragg reflections from the FTO coated glass substrate; bottom green markers highlight the Bragg reflection positions associated with VO$_2$(M1) (JCPDS card number 01-82-0661) (b) Core level XPS spectra of V 2p$_{3/2}$ and O 1s. Inset shows the high resolution valence band region of VO$_2$(M1) XPS spectra.

**Fig. 3.** SEM images of VO$_2$ powder: (a) at low magnification, (b) at higher magnification; screen printed VO$_2$ thin films: (c) at low magnification, (d) at higher magnification.

**Fig. 4.** The J-V curves of the DSSCs fabricated with VO$_2$ and Pt counter electrodes, respectively.

**Fig. 5.** Nyquist plots of full cells assembled with VO$_2$ and Pt counter electrodes, respectively.

**Fig. 6.** Cyclic voltammograms of VO$_2$ and Pt counter electrodes measured at a fixed scan rate of 50 mVs$^{-1}$ using three electrode configurations.
Fig. 2

(a) Powder 
Film 
Bragg reflections 
* FTO glass

Two theta (degree)

Intensity (a.u.)

0 2000 5600 5610 5620 5630 5640 5650

(011) (110) (-102) (002) (-211) (012) (212) (-302) (032) (-221) (222) (022) (-321) (331) (221) (-302) (012) (002) (-211) (102) (022) (221) (-321) (331) (221) (-302) (012) (002) (-211) (102) (022) (221) (-321) (331) (221) (-302) (012) (002) (-211) (102) (022) (221) (-321) (331) (221) (-302) (012) (002) (-211) (102) (022) (221) (-321) (331) (221) (-302) (012) (002) (-211) (102)

(b) Data 
Fitting 
V 2p3/2 (V4+) 
V 2p3/2 (V5+) 
V O1s 
C O1s 

Binding energy (eV)

0 514 516 518 520 522 524 526 528 530 532 534 536 538 540

Intensity (a.u.)

0 4000 8000 12000 16000

V 3d

O 2p

O 1s

Inset: V 2p3/2 (V4+)
Fig. 3
Fig. 4

Current density (mA cm$^{-2}$) vs. Voltage (V).

- **Pt** (circles)
- **VO$_2$** (stars)
Fig. 5

(a) $-Z''(\Omega)$ vs. $Z'(\Omega)$ for Pt

(b) $-Z''(\Omega)$ vs. $Z'(\Omega)$ for VO$_2$
Fig. 6

![Graph showing current vs. voltage for different materials (Pt and VO₂). The graph displays two oxidation (Ox-1, Ox-2) and two reduction (Red-1, Red-2) peaks. The x-axis represents voltage vs. Ag/AgCl (V), and the y-axis represents current (mA).]