

Short communication

Synthesis of vanadium pentoxide powders with enhanced surface-area for electrochemical capacitors

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Abstract

Single-phase, chemically pure vanadium pentoxide (V_2O_5) powders are prepared by co-precipitation and further calcination at 300 °C. The materials obtained are agglomerated in sub-micron particles, and BET analysis shows that the as-prepared V_2O_5 powders have a high specific surface-area of 41 m² g⁻¹. V_2O_5 shows the highest capacitance in 2 M KCl electrolyte when compared with other electrolytes such as 2 M NaCl and 2 M LiCl. It yields a maximum specific capacitance of 262 F g⁻¹. The higher specific surface-area may be the reason for the high capacitance compared with previously published results.

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1. Introduction

Oxides of vanadium are of considerable interest because of their phase transformations as well as their uses in energy-related devices [1–3]. Vanadium pentoxide (V_2O_5) has become a compound of particular interest in recent years because of its potential application in optical switching devices [4], and electrochromic devices [5–7], as well as a reversible cathode material for lithium batteries [8,9]. The compound is also a promising electrode material for electrochemical capacitors (EC) because of its low cost and its ability to exist in different oxidation states.

To date, the best specific capacitance value of 720 F g⁻¹ has been obtained by using amorphous ruthenium oxide as an electrode at a 2 mV s⁻¹ scan rate in H_2SO_4 electrolyte [10]. This material is, however, very expensive and thus many efforts have been made to find a suitable alternative material. Only a very few investigations have been performed on V_2O_5 as an electrode material for electrochemical capacitors [11–13]. It has been prepared by quenching V_2O_5 fine powders at 950 °C in a bath of de-ionized water [11]. The material showed an ideal capacitance curve in an aqueous KCl electrolyte under cyclic voltammetric conditions, and a specific capacitance of 346 F g⁻¹ at a pH of

2.32 was reported. In a different approach [13], V_2O_5 sol was synthesized by reacting metallic vanadium with 30% H_2O_2 . The material was mixed with carbon to prepare composite electrodes for use in non-aqueous electrolytes. This material did not, however, show ideal capacitance, and the authors did not mention the specific capacitance in their paper. Recently, nano-porous layer-structured V_2O_5 has been prepared by the sol–gel method [14]. This material gave the highest capacitance (214 F g⁻¹) in 2 M KCl electrolyte when compared with other electrolytes such as NaCl and LiCl.

In the work, reported here, a different, time-efficient method based on a co-precipitation and calcination technique is used to prepare sub-micron or nano-crystalline V_2O_5 powders. Their physical and electrochemical properties as electrode materials for electrochemical capacitors are systematically tested.

2. Experimental

Commercial Aldrich vanadium trichloride (VCl_3) and ammonium hydroxide (NH_4OH) were used as starting materials. A 0.2 M vanadium trichloride aqueous solution and a 0.2 M ammonium hydroxide aqueous solution were prepared for co-precipitation. The ammonium hydroxide was added dropwise to the vanadium trichloride solution under rigorous stirring. The precipitate was filtered and washed several times with distilled

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water to remove any soluble products. Finally, the precipitate was heat-treated at 300 °C in air for 1 h to obtain the V₂O₅ powders.

The as-prepared V₂O₅ was characterized by X-ray diffraction. The morphology of the oxide powders was observed by scanning electron microscopy (SEM). The specific surface-area of the powders was determined by the gas sorption technique using the BET method.

Beaker-type three-electrode test cells were fabricated to evaluate the electrochemical properties of the V₂O₅ powders. The working electrode was made by dispersing 67 wt.% V₂O₅ material, 25 wt.% carbon black, and 8 wt.% polyvinylidene difluoride (PVDF) binder in dimethyl phthalate solvent to form a slurry that was then spread on to a platinum foil. A platinum foil was used as a counter electrode. All potentials are reported with respect to a saturated calomel reference electrode (SCE). The electrolytes were NaCl, KCl and LiCl. Cyclic voltammetry (CV) was conducted over a voltage range of −0.2 to 0.7 V at varying scan rates.

3. Results and discussion

A typical XRD pattern for the V₂O₅ powders is shown in Fig. 1. The powders have a single-Scherbinaite phase with an orthorhombic structure (PDF card 41-1426) and lattice parameters $a = 1.1516$ nm, $b = 0.332$ nm, and $c = 0.43727$ nm. The crystal size of the V₂O₅ crystallites as evaluated by the well-known Scherrer formula and found to be about 70 nm.

The morphological features of the V₂O₅ powders observed at different magnifications are shown in Fig. 2. The powders consist of agglomerates with different shapes (Fig. 2(a)). The agglomerates themselves consist of very fine particles (Fig. 2(b and c)) with sizes under 100 nm. Their appearance suggests a highly-developed surface-area, which has been confirmed by BET. A specific surface-area of 41 m² g^{−1} was calculated from a multi-point BET measurement.

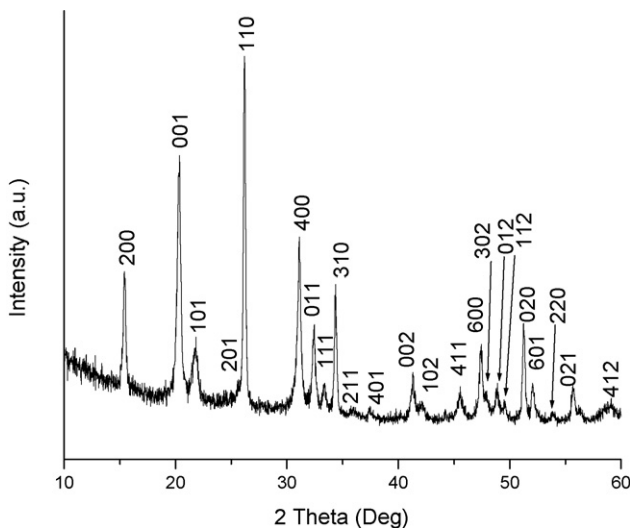
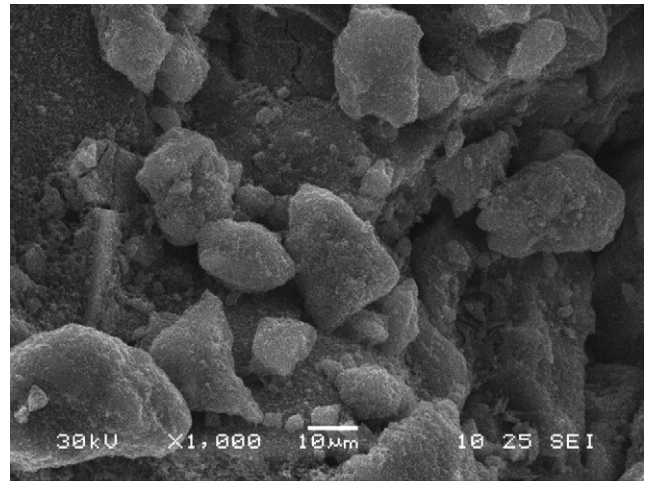
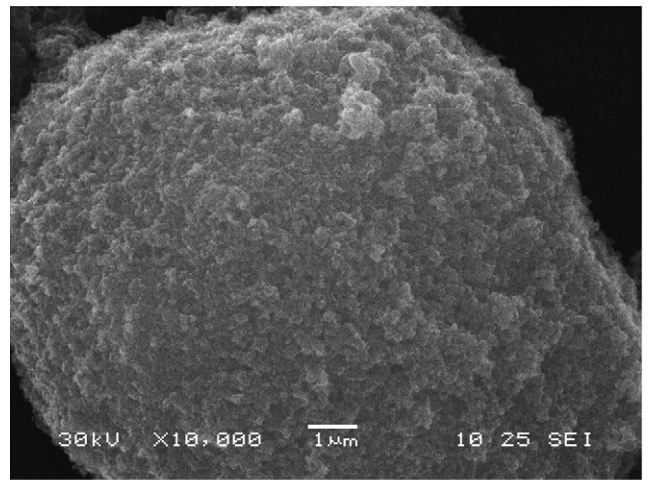


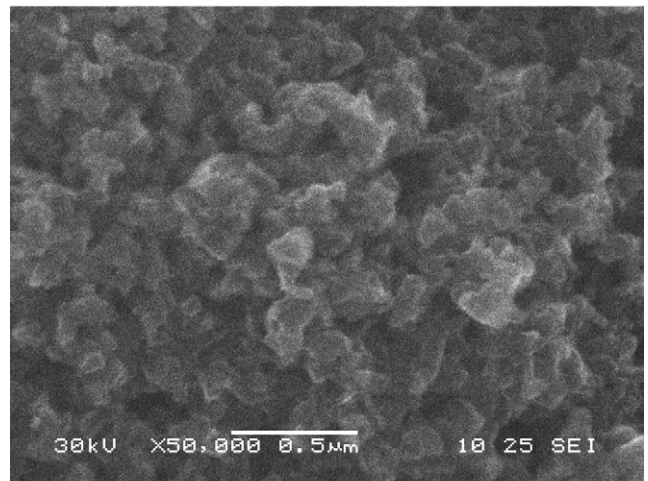
Fig. 1. X-ray diffraction pattern of as-prepared V₂O₅.



(a)



(b)



(c)

Fig. 2. Scanning electron micrographs of as-prepared V₂O₅ at different magnifications: (a) 1000×, (b) 20,000×, and (c) 50,000×.

Fig. 3 shows cyclic voltammetric curves of V₂O₅ in 2 M KCl at different scan rates. The shapes of the CV curves are significantly influenced by the scan rate. At a low rate (5 mV s^{−1}), the CV curve shows a near-ideal rectangular shape. This indi-

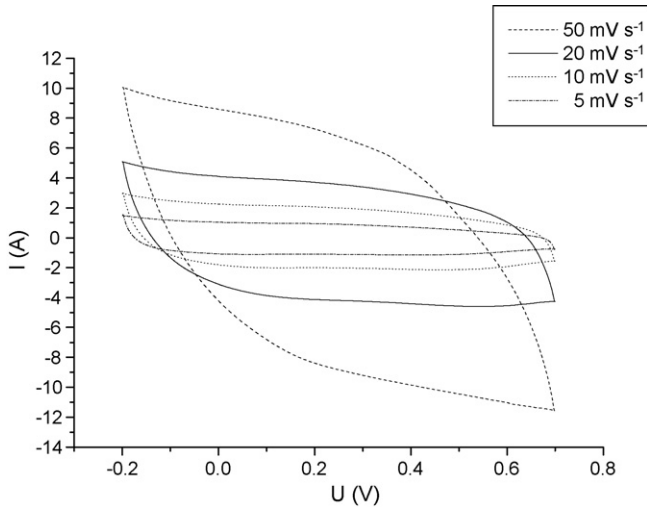


Fig. 3. Cyclic voltammograms of V₂O₅ in 2 M KCl at various scan rates.

states that charging and discharging take place at a constant rate over the applied voltage range [15]. A specific capacitance of 262 F g⁻¹ was obtained for V₂O₅ powders at a 5 mV s⁻¹ scan rate. Fig. 4 gives a plot of specific capacitance as a function of scan rate in 2 M KCl electrolyte. The specific capacitance gradually decreases as the scan rate is increased from 5 to 50 mV s⁻¹. This may be because at high scan rates, diffusion limits the movement of K⁺ ions due to the time constraint, and only the outer active surface is utilized for charge storage. At lower scan rates, however, all the active surface-area can be utilized for charge storage [14].

Cyclic voltammetric curves of V₂O₅ in 2 M KCl, 2 M NaCl, and 2 M LiCl at 5 mV s⁻¹ are presented in Fig. 5. As is evident from the data, V₂O₅ yields the highest specific capacitance in 2M KCl electrolyte. It is interesting to note that V₂O₅ gives similar specific capacitance values of 166 and 160 F g⁻¹ in 2 M NaCl and 2 M LiCl electrolytes, respectively, despite the difference in the size of the sphere of hydration of Na⁺ and Li⁺ ions. The specific capacitances of V₂O₅ in different electrolytes are compared in Table 1 with values obtained from the literature [14]. A higher specific capacitance is achieved for the present V₂O₅, possibly because this material has a higher specific surface-

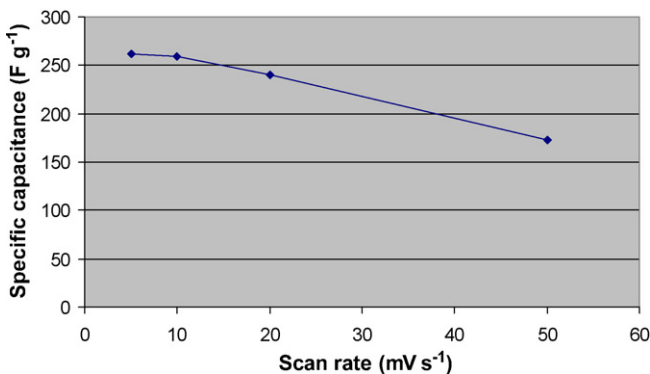


Fig. 4. Specific capacitance vs. scan rate.

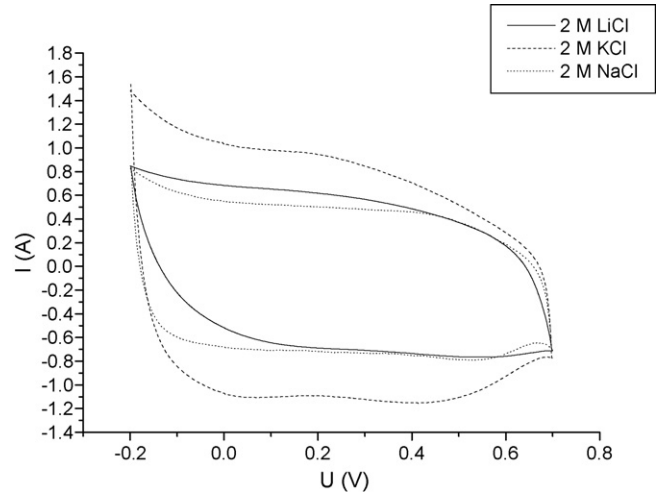


Fig. 5. Cyclic voltammograms of V₂O₅ in different electrolytes.

Table 1

Comparison of specific capacitance values of present V₂O₅ materials with those reported in the literature for different electrolytes at 5 mV s⁻¹

Electrode material	Specific surface-area (m ² g ⁻¹)	Electrolyte	Specific capacitance (F g ⁻¹)	Reference
V ₂ O ₅	41	2 M KCl	262	Present study
V ₂ O ₅	41	1 M KCl	201	Present study
V ₂ O ₅	41	2 M NaCl	166	Present study
V ₂ O ₅	41	2 M LiCl	160	Present study
V ₂ O ₅	7	2 M KCl	214	[14]
V ₂ O ₅	7	2 M NaCl	114	[14]
V ₂ O ₅	7	2 M LiCl	122	[14]

area (41 m² g⁻¹) than that (7 m² g⁻¹) previously reported in ref. [14].

Cyclic voltammetric curves of V₂O₅ in 2 M KCl and 1 M KCl at 5 mV s⁻¹ are given in Fig. 6. The specific capacitance of V₂O₅ increases when the concentration of KCl is increased.

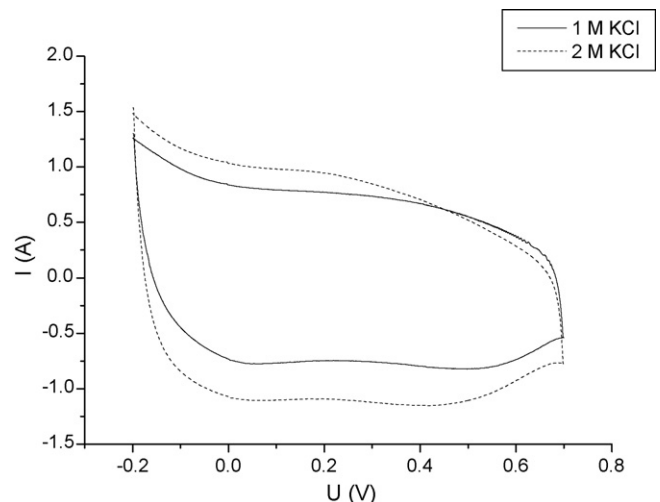


Fig. 6. Cyclic voltammetric curves of V₂O₅ in 2 M KCl and 1 M KCl at a 5 mV s⁻¹.

This may be because a lower concentration of KCl has a higher electrolyte resistance.

4. Summary

Single-phase, crystalline V_2O_5 powders are obtained by co-precipitation and calcined by further thermal treatment at 300°C . Scanning electron microscopic analysis reveals that the structure consists of agglomerated sub-micron or nano-crystalline particles. The BET result shows that the prepared V_2O_5 powders have a high specific surface-area of $41\text{ m}^2\text{ g}^{-1}$. The V_2O_5 yields a maximum specific capacitance of 262 F g^{-1} in 2 M KCl electrolyte, i.e., higher than in other electrolytes such as 2 M NaCl and 2 M LiCl . The superior specific capacitance of the present V_2O_5 compared with that reported in the literature can be explained in terms of higher specific surface-area.

Acknowledgement

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