

Short communication

# Hydrothermal synthesis of $\text{SnO}_2\text{-V}_2\text{O}_5$ mixed oxide and electrochemical screening of carbon nano-tubes (CNT), $\text{V}_2\text{O}_5$ , $\text{V}_2\text{O}_5\text{-CNT}$ , and $\text{SnO}_2\text{-V}_2\text{O}_5\text{-CNT}$ electrodes for supercapacitor applications

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## Abstract

Nano-scaled  $\text{SnO}_2\text{-V}_2\text{O}_5$  mixed oxide is synthesized by a hydrothermal method in an autoclave. For comparative evaluation,  $\text{V}_2\text{O}_5$  single oxide is prepared by a conventional process from ammonium vanadate. The capacitive behaviour of the following electrodes is studied by cyclic voltammetry in 0.1 M KCl solutions: carbon nano-tubes (CNT),  $\text{V}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5\text{-CNT}$ , and  $\text{SnO}_2\text{-V}_2\text{O}_5\text{-CNT}$ . At a scan rate of  $100\text{ mV s}^{-1}$ , the  $\text{SnO}_2\text{-V}_2\text{O}_5\text{-CNT}$  electrode provides the best performance, viz.,  $121.4\text{ F g}^{-1}$ . The nano-scaled mixed oxide is characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Raman spectra.

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**Keywords:** Hydrothermal synthesis; Nano-mixed oxides; Electrochemical capacitor; Carbon nano-tubes; Cyclic voltammetry

## 1. Introduction

Electrochemical capacitors (ECs), or supercapacitors, have attracted much attention in recent times. In an attempt to increase the performance of ECs, various permutations and combinations of metal oxides and other organic and inorganic moieties have been investigated. Such materials are added either *in situ* during synthesis or mixed during the electrode preparation. Thin-film microbatteries and thin-film micro-supercapacitors, which are widely used as power sources in micro-electronic mechanical systems and nano-electronic mechanical systems, have stimulated tremendous interest to create and identify new nano-materials based on metal oxides. Electrochemical capacitors in combination with rechargeable batteries form a powerful hybrid energy-storage device. Prototypes made of ruthenium and tantalum oxides proved highly successful and have preceded to commercialization. As ruthenium is highly expensive, alternatives are being sought to reduce the cost factor. This has led to studies of the combination of ruthenium oxide with metal

oxides such as  $\text{TiO}_2$ ,  $\text{VO}_x$ ,  $\text{MoO}_3$ ,  $\text{SnO}_2$ ,  $\text{WO}_3$  and  $\text{CaO}$  in the form of thin films [1–7]. In addition, other metal oxides and mixed metal oxides have been prepared and evaluated, e.g.,  $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$  [8], Ppy (polypyrrole)/ $\text{Al}_2\text{O}_3/\text{Al}$  [9], amorphous  $\text{MnO}_2$  [10], hydrous  $\text{IrO}_2$  [11],  $\text{SrCoO}_{2.5}$  [12], Sb-doped  $\text{SnO}_2$  [13],  $\text{Ti/RhO}_x + \text{Co}_3\text{O}_4$  [14],  $\text{NiO/RuO}_2$  [15],  $\text{Ir}_{0.3}\text{Mn}_{0.7}\text{O}_2$  [16],  $\text{SrRuO}_3$  [17], amorphous hydrous  $\text{MnO}_2/\text{carbon}$  [18],  $\text{NiO/activated carbon}$  [19] and carbon nano-tubes (CNT) in anodized aluminum oxides [20]. Such investigations seek a compromise between the cost and the performance of ECs.

Vanadium pentoxide ( $\text{V}_2\text{O}_5$ ), in particular, has been widely examined as an electrode material for ECs that use organic electrolytes [21–23]. Since  $\text{V}_2\text{O}_5$  has a modest electronic conductivity, composites with metal fibres or carbonaceous materials have been prepared in an attempt to improve electrode performance [24–29]. By contrast, these are very few reports of the pseudo-capacitive behaviour of this oxide. Lee and Goodenough [30] prepared amorphous  $\text{V}_2\text{O}_5$  by quenching  $\text{V}_2\text{O}_5$  powders heated at  $950^\circ\text{C}$  and studied the material in aqueous KCl solutions under cyclic voltammetric conditions. The specific capacitance reported was  $350\text{ F g}^{-1}$  [30]. Reddy and Reddy [31] prepared nano-porous  $\text{V}_2\text{O}_5$  by a sol-gel method

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and obtained a maximum specific capacitance of  $214 \text{ F g}^{-1}$  at a scan rate of  $5 \text{ mV s}^{-1}$  in  $2 \text{ M KCl}$  solutions. They reported a decrease in capacitance after 100 cycles under the same experimental conditions. In catalytic applications, it is known that  $\text{SnO}_2$  is different from other more conventional supports; it exhibits efficient semi-conductivity together with conventional redox properties. In combination with  $\text{V}_2\text{O}_5$ ,  $\text{SnO}_2$  forms a catalyst that is capable of promoting many organic conversions. In effect,  $\text{SnO}_2$  enhances the use ratio of  $\text{V}_2\text{O}_5$  to a different dimension [32,33].

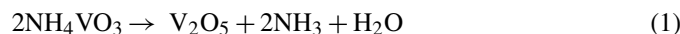
The focus of investigation reported here is the synthesis and characterization of a nano-scale  $\text{SnO}_2\text{-V}_2\text{O}_5$  mixed oxide, by a simple hydrothermal method, for application in supercapacitors. Integral  $\text{V}_2\text{O}_5$  is also prepared, by a conventional combustion method, for comparative evaluation. Electrochemical characterization of the single and the mixed oxides with and without added CNT is undertaken by means of cyclic voltammetry in order to screen the effect of CNT and  $\text{SnO}_2$  on the faradic pseudo-capacitive response of  $\text{V}_2\text{O}_5$ . The use of CNTs as the best substrate material has been emphasized in recent publications by Kim et al. [34,35]. The electrochemical performance of  $\text{V}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5\text{-CNT}$ ,  $\text{SnO}_2\text{-V}_2\text{O}_5$  and  $\text{SnO}_2\text{-V}_2\text{O}_5\text{-CNT}$  is examined in  $0.1 \text{ M KCl}$  solution.

## 2. Experimental

### 2.1. Synthesis of materials

#### 2.1.1. $\text{V}_2\text{O}_5$ by solid-state method

Solid  $\text{NH}_4\text{VO}_3$  (5.8 g) was taken in a alumina crucible and calcined at  $500^\circ\text{C}$  in a muffle furnace for 3 h in the presence of air.  $\text{NH}_4\text{VO}_3$  decomposes to yield  $\text{V}_2\text{O}_5$ , i.e.,



#### 2.1.2. $\text{SnO}_2\text{-V}_2\text{O}_5$ by hydrothermal method

$\text{NH}_4\text{VO}_3$  (0.05 mol) and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (0.05 mol) were dissolved in 250 ml of water, urea (0.2 mol) was added, and the homogeneous mixture was transferred to an autoclave. The solution was allowed to reach to  $180^\circ\text{C}$  within an hour (ramp time). The reaction was held at this temperature for 2 h (soak time) with an *in situ* pressure of 12 atm. After 2 h, the solution was cooled to room temperature and the product was filtered, washed with water and acetone, and dried at  $110^\circ\text{C}$  in a air oven. The experimental solution was initially acidic ( $\text{pH} \sim 4$ ) but finally became alkaline ( $\text{pH} \sim 8$ ). The resulting powder was calcined at  $500^\circ\text{C}$  for 3 h.

#### 2.1.3. Electrodes

Carbon nano-tubes and the oxides (both simple and mixed) were taken in a mole ratio of 1:10 and mixed thoroughly in a mortar prior to fixing on the surface of a graphite electrode that was impregnated with paraffin. The following electrode materials were prepared:  $\text{V}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5\text{-CNT}$ ,  $\text{SnO}_2\text{-V}_2\text{O}_5$  and  $\text{SnO}_2\text{-V}_2\text{O}_5\text{-CNT}$ .

### 2.2. Instrumentation

All electrochemical experiments were conducted with a PGSTAT 30 Autolab system (Ecochemie, Utrecht, The Netherlands), which was connected to a PC running with EcoChemie GPES software. The reference electrode was  $\text{Ag}|\text{AgCl}$  (3 M KCl), the counter electrode was a platinum foil, and the electrolyte solution was  $0.1 \text{ M KCl}$ . A paraffin-impregnated graphite electrode (PIGE) was used as the working electrode. A few micrograms of the mixed oxide nano-particles were placed on a clean glass plate and the PIGE electrode was pressed over the nano-material so that it was mechanically transferred to the tip of the electrode [36].

Powder X-ray diffraction (XRD) data from the samples were obtained by means of a Siemens D 5000 X-ray diffractometer with Bragg–Brentano geometry and  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Transmission electron microscope (TEM) images were obtained with a PHILIPS Tecnai-12 FEI instrument operated at an accelerating voltage of 100 kV.

## 3. Results and discussion

### 3.1. Synthesis and characterization of nano- $\text{SnO}_2\text{-V}_2\text{O}_5$

The XRD patterns of as-prepared and calcined  $\text{SnO}_2\text{-V}_2\text{O}_5$  mixed oxide prepared by urea hydrolysis under hydrothermal conditions are given in Fig. 1. The XRD peaks of the as-prepared sample can be indexed to both  $\text{SnO}$  and  $\text{SnO}_2$  peaks;  $\text{SnO}$  is present as major phase and the peaks are sharper, which indicates the good crystallinity of the particles.  $\text{SnO}_2$  is present as a minor phase and the broadened peaks reveal the poorly crystalline nature of particles. In the calcined sample, the  $\text{SnO}$  phase disappears, as expected, and the  $\text{SnO}_2$  develops as the major phase; the peaks appear with high intensity and are much more broadened than for the as-prepared sample. This is an indication that the  $\text{SnO}_2$  particles are of nano-scale dimensions, which is confirmed by scanning electron microscope (SEM) images (Fig. 3). Quite interestingly, the as-prepared mixed oxide

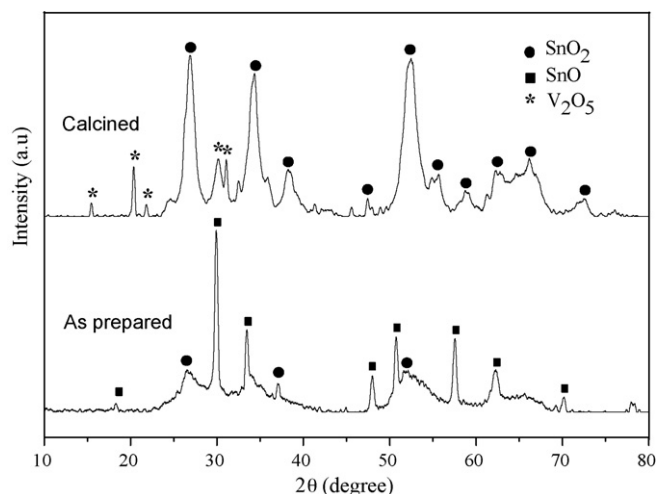


Fig. 1. XRD patterns of as-prepared and calcined  $\text{SnO}_2\text{-V}_2\text{O}_5$  mixed oxide prepared by urea hydrolysis.

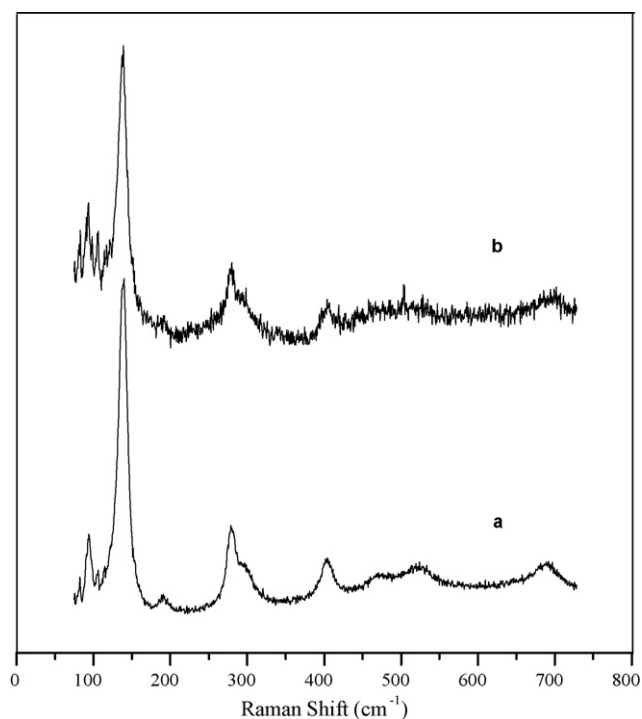


Fig. 2. Raman spectrum recorded for (a) as-prepared; (b) calcined  $\text{SnO}_2\text{-V}_2\text{O}_5$  mixed oxide.

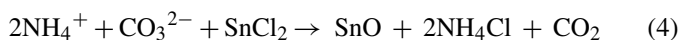
does not show any peaks pertaining to  $\text{V}_2\text{O}_5$ , though its presence was confirmed by Raman spectra (Fig. 2). By contrast, the calcined sample displays peaks pertaining to  $\text{V}_2\text{O}_5$ , and thus, confirms the phase transformation from amorphous to crystalline.

The Raman spectrum recorded for the as-prepared mixed oxide is given in Fig. 2(a). These are bands typical of  $\text{V}_2\text{O}_5$  centred at 103, 145, 195, 282, 303, 403, 483, 529 and  $700\text{ cm}^{-1}$  and an identical spectrum (Fig. 2(b)) is obtained for the calcined mixed oxide. The Raman bands are in agreement with an earlier study [37]. This result confirms the formation of amorphous  $\text{V}_2\text{O}_5$  in the mixed oxide, and that calcination transforms the amorphous phase to the crystalline counterpart.

Scanning electron micrographs of  $\text{V}_2\text{O}_5$  and the calcined  $\text{SnO}_2\text{-V}_2\text{O}_5$  mixed oxide are shown in Fig. 3(a) and (b), respectively. There is a marked difference in morphology between these two powders. Whereas,  $\text{V}_2\text{O}_5$  forms well-shaped platelets with irregular shapes,  $\text{SnO}_2\text{-V}_2\text{O}_5$  exists as an amorphous phase in the form of fine particles grouped together as clusters with pores between both the particles and the clusters. The distribution of the nano-particles is seen more clearly in the TEM image presented in Fig. 3(c). This shows a cloud of nano-metric ( $\sim 10\text{ nm}$ ) particles that touch each other to leave free spaces so that the mass appears very porous. The particles have a very broad size-distribution with no faceted aggregates. The network of particles contains intermittent voids.

The hydrothermal synthesis of  $\text{SnO}_2\text{-V}_2\text{O}_5$  mixed oxide is interesting in that  $\text{V}_2\text{O}_5$  has been obtained as an amorphous phase, which is usually achieved by the sol-gel method [38,39]. The fact that XRD peaks pertaining to this oxide were not observed for the as-prepared sample was not unexpected as

we experienced the same feature in our previous synthesis of  $\text{SnO}_2\text{-Al}_2\text{O}_3$  by this route [40]. We proved the presence of alumina by Al MAS NMR and EDAX measurements. This dominance of  $\text{SnO}/\text{SnO}_2$  in the two mixed oxides is not clear to us. The reactions responsible for the production of  $\text{SnO}_2\text{-V}_2\text{O}_5$  in the autoclave may be written as:



### 3.2. Cyclic voltammetric studies

Cyclic voltammograms (CVs) recorded for CNT immobilized on the surface of PIGE are given in Fig. 4. The  $I\text{-}V$  curves are quite rectangular as expected for typical capacitive behaviour. Sinusoidal waves are not observed at scan rates of  $0.05$  and  $0.1\text{ V s}^{-1}$ . The probable reason is that each CNT acts as a single electrode at these scan rates, and that the mass transfer experienced by a single CNT is in synchronization with the  $I\text{-}V$  signal therefore provides the same signature. At high and low scan rates, the signals are averaged so that the CVs look like normal ones. The specific capacitance decreases slightly with continuous cycling, as shown in Table 1. For the single  $\text{V}_2\text{O}_5$  oxide, the CV responses recorded for the 1st and 100th scan are presented in Fig. 5. The initial scan has a near-rectangular shape which indicates ideal capacitive behaviour. These features disappears with continuous cycling; in the 100th scan, the CV curve looks like a spindle and this could be due to the resistance offered by the surface oxide films.

Similar CV responses have been observed for  $\text{V}_2\text{O}_5$  in much higher KCl (1 and 2 M) concentrations [30]. Amorphous  $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  was found to have specific capacitance of  $286.3\text{ F g}^{-1}$  in an electrolyte solution with pH 6.67 and  $346.4\text{ F g}^{-1}$  in an electrolyte solution with pH 2.32. The electrolyte solution was 2 M KCl and the scan rate was  $5\text{ mV s}^{-1}$ . At the same low scan rate of  $5\text{ mV s}^{-1}$  and in 1 M KCl solutions, a specific capacitance of  $214\text{ F g}^{-1}$  has been reported [31]. We have obtained a lower value but the scan rate is  $100\text{ mV s}^{-1}$  and the KCl solutions are more dilute. It is highly unfortunate that there is no common platform on which the specific capacitances of electrode materials may be compared. Thus, meaningful comparisons are difficult as performance levels depend on many factors such as concentration, pH and identity of the electrolyte, scan rate, nature of technique (whether cyclic voltammetry or

Table 1  
Specific capacitance values calculated from cyclic voltammograms for 1st and 100th scans; scan rate =  $100\text{ mV s}^{-1}$

Electrode	Anodic scan ( $\text{F g}^{-1}$ )		Cathodic scan ( $\text{F g}^{-1}$ )	
	1	100	1	100
CNT	2.40	2.07	2.12	2.06
$\text{V}_2\text{O}_5$	7.65	12.09	3.69	12.18
$\text{CNT} + \text{V}_2\text{O}_5$	26.28	44.69	18.96	47.21
$\text{CNT} + \text{V}_2\text{O}_5 + \text{SnO}_2$	121.39	104.18	119.85	104.45

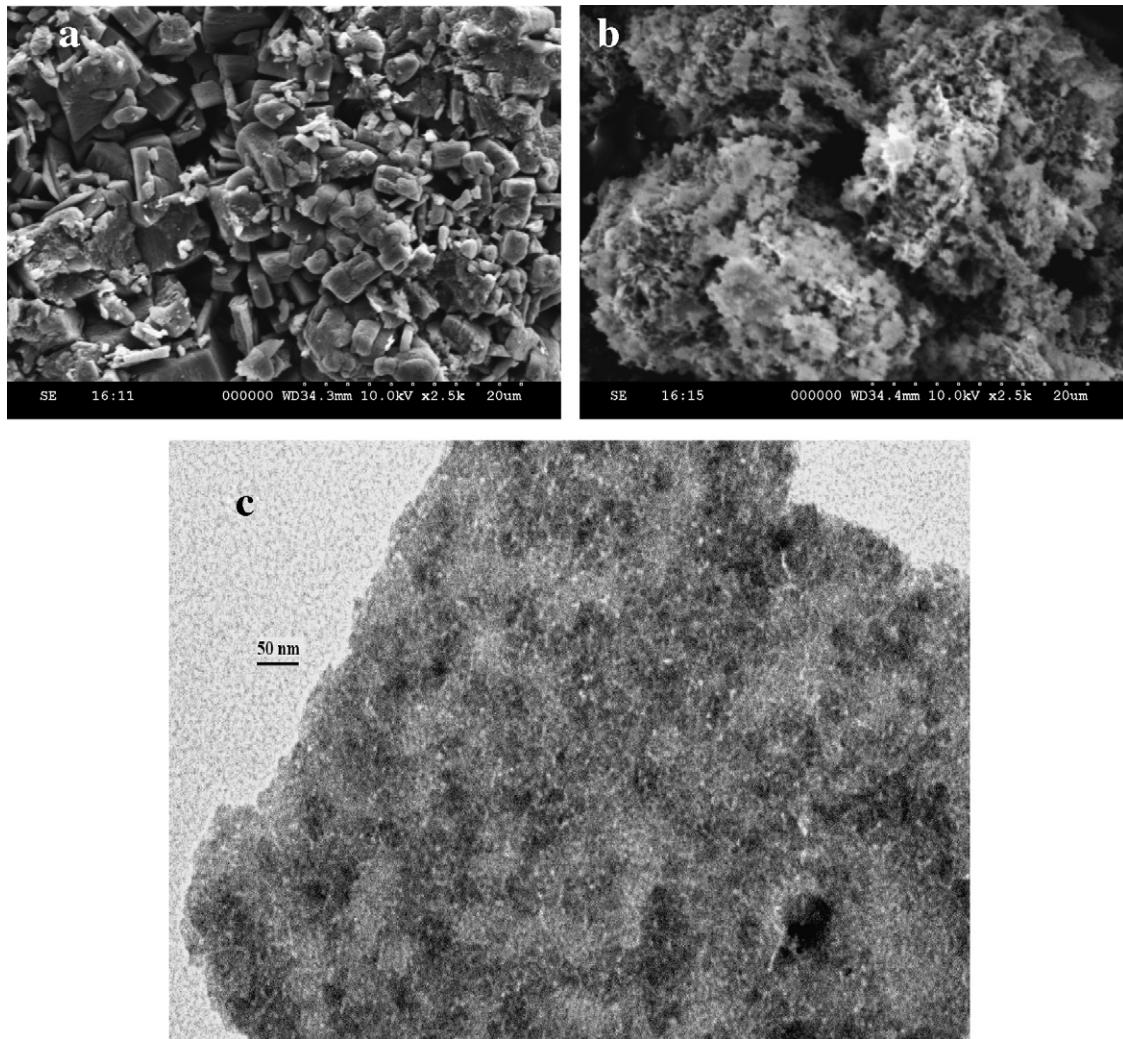


Fig. 3. SEM images of (a) single  $V_2O_5$ , (b) calcined  $SnO_2-V_2O_5$  mixed oxide, (c) TEM image of calcined  $SnO_2-V_2O_5$  mixed oxide.

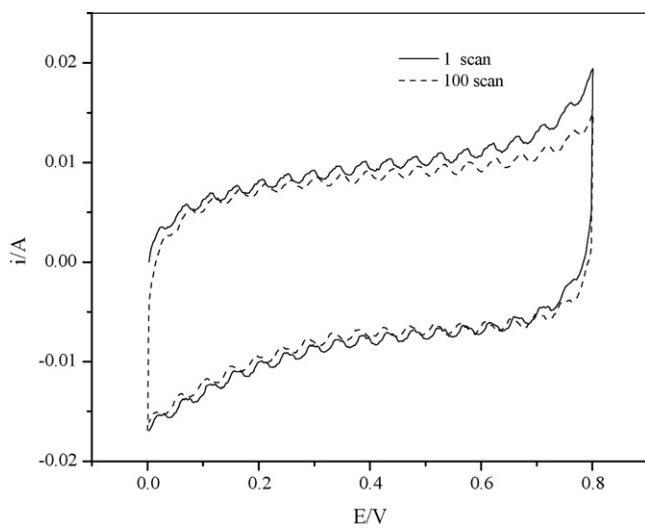


Fig. 4. Cyclic voltammograms of CNT immobilized on PIGE and recorded in 0.1 M KCl solutions; scan rate =  $0.1 \text{ V s}^{-1}$ .

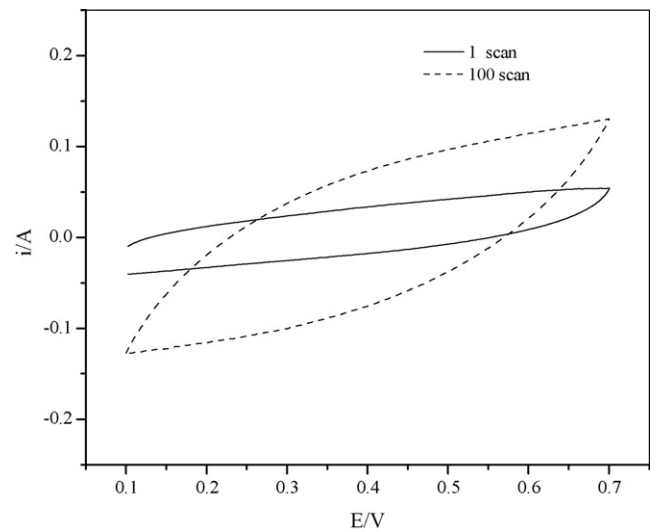


Fig. 5. Cyclic voltammograms of single  $V_2O_5$  immobilized on PIGE electrode and recorded in 0.1 M KCl solutions; scan rate =  $0.1 \text{ V s}^{-1}$ .



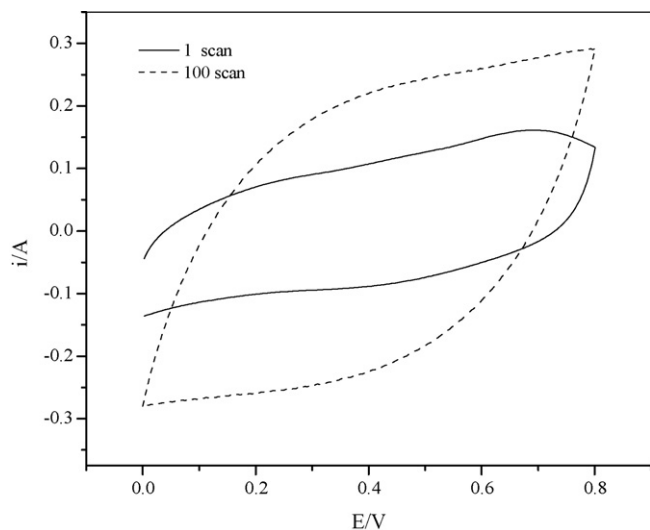


Fig. 6. Cyclic voltammograms of composite CNT-V<sub>2</sub>O<sub>5</sub> electrode recorded in 0.1 M KCl solutions; scan rate = 0.1 V s<sup>-1</sup>.

chronopotentiometry), amorphous or crystalline phase, electrode fabrication, and method of preparation.

The CVs for the composite CNT-V<sub>2</sub>O<sub>5</sub> electrode are shown in Fig. 6. The behaviour synchronizes with that for CNT on the initial scan but changes to that of V<sub>2</sub>O<sub>5</sub> after 100 cycles. The specific capacitance increased two-fold on cycling; a characteristic feature similar to that of single V<sub>2</sub>O<sub>5</sub>. The addition of CNT (CNT:V<sub>2</sub>O<sub>5</sub> = 1:10) increases the capacitance to almost three-fold above that of simple oxide (Table 1). This advantage of CNT is well exploited in supercapacitor electrodes that employ organic solvents. The CV behaviour of the composite CNT-V<sub>2</sub>O<sub>5</sub>-SnO<sub>2</sub> mixed oxide in 0.1 M KCl solutions is presented in Fig. 7. The specific capacitance increases by almost five-fold on the initial scan compared with that of the CNT-V<sub>2</sub>O<sub>5</sub> electrode; in the cathodic scan, the increase is six-fold. The observed decrease in capacitance on the anodic and cathodic scans over 100 cycles is uniform for all electrode types.

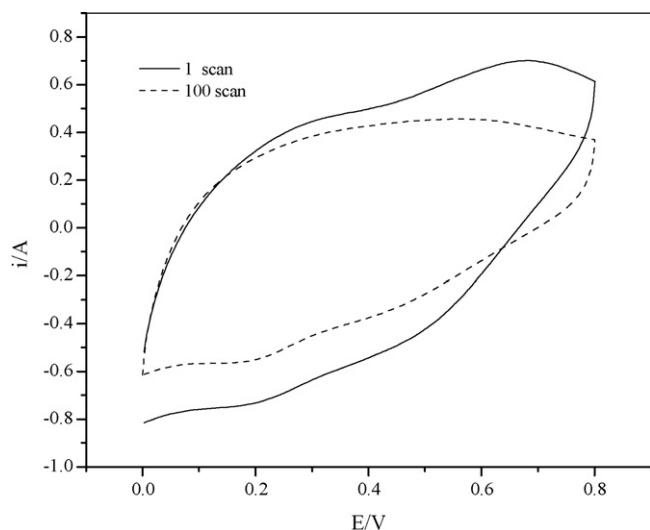


Fig. 7. Cyclic voltammograms of CNT-V<sub>2</sub>O<sub>5</sub>-SnO<sub>2</sub> electrode recorded in 0.1 M KCl solutions; scan rate = 0.1 V s<sup>-1</sup>.

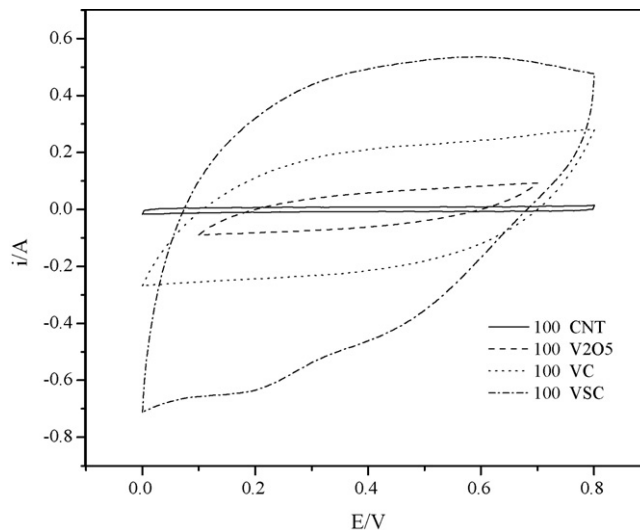


Fig. 8. Comparison of cyclic voltammograms of CNT, V<sub>2</sub>O<sub>5</sub>, CNT-V<sub>2</sub>O<sub>5</sub>, CNT-V<sub>2</sub>O<sub>5</sub>-SnO<sub>2</sub> electrodes at scan rate of 0.1 V s<sup>-1</sup>.

A comparative evaluation of representative CVs of CNT, V<sub>2</sub>O<sub>5</sub>, CNT-V<sub>2</sub>O<sub>5</sub> and CNT-V<sub>2</sub>O<sub>5</sub>-SnO<sub>2</sub> is given in Fig. 8. It is obvious that CNT-V<sub>2</sub>O<sub>5</sub>-SnO<sub>2</sub> is the best electrode. The presence of SnO<sub>2</sub> as a mixed oxide helps to increase the electronic and redox properties of V<sub>2</sub>O<sub>5</sub> but the decrease in charge with cycling indicates the formation of a passive film that is resistive in nature.

The higher specific capacitance of CNT-V<sub>2</sub>O<sub>5</sub>-SnO<sub>2</sub> demonstrates that the electronic properties can be changed favourably with a suitable choice of the additive in the electrode material. Though this combination gave the highest value, the capacitance values observed for the individual components as against their mutual combination is also interesting. Rather as a single entities, CNT and V<sub>2</sub>O<sub>5</sub> together gave better values (19–26 F g<sup>-1</sup> on the initial scan and 45–47 F g<sup>-1</sup> on the 100th scan). As the capacitance value of CNT does not change with cycling, this improvement could be attributed to V<sub>2</sub>O<sub>5</sub>, which experiences an increase in capacitance even as a single entity. For a typical supercapacitor electrode material, such behaviour is not expected. In the case of pseudo-capacitors where the electrodes exhibit both faradic and non-faradic capacitances, such redox behaviour is understandable. Hence, in the electrode CNT-V<sub>2</sub>O<sub>5</sub>, CNT contributes to non-faradic double-layer capacitance while V<sub>2</sub>O<sub>5</sub> contributes to both faradic and non-faradic capacitances. For the CNT-V<sub>2</sub>O<sub>5</sub>-SnO<sub>2</sub> electrode, both V<sub>2</sub>O<sub>5</sub> and SnO<sub>2</sub> contribute to both kinds of capacitance as visualized by the increased specific capacitance values with cycling.

The most unexpected result is the low value of specific capacitance obtained for CNT immobilized on PIGE in 0.1 M KCl solutions. Although the CV response is that of a perfect double-layer capacitor, the values are disappointing. The CV response of CNTs in organic solvents is well established and high capacitances have been reported. Since no pretreatment was done during electrode preparation in this study, the possibility that the surface area becoming damaged can be excluded. The possibility that the electrode surface becomes passivated in dilute KCl solutions is also not valid. In aqueous solutions, CNT may

not induce charge separation at the interface as in non-aqueous solvents but we can offer no explanation for such behaviour.

#### 4. Conclusions

In this communication,  $\text{SnO}_2\text{-V}_2\text{O}_5$  mixed oxide is synthesized by a hydrothermal method in an autoclave. The as-prepared  $\text{SnO}/\text{SnO}_2$  particles in the mixed oxide are in the nano-scale range while  $\text{V}_2\text{O}_5$  exists as an amorphous phase. A composite  $\text{SnO}_2\text{-V}_2\text{O}_5\text{-CNT}$  electrode is found to give the highest specific capacitance. The presence of  $\text{SnO}_2$  increases the electronic properties of vanadium oxide and improves the capacitive behaviour.

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