

## High Rate Magnesium Intercalation into V<sub>2</sub>O<sub>5</sub>/Carbon Composites

Daichi Imamura, Mitsuhiro Hibino\*, Masaru Miyayama and Tetsuichi Kudo

Institute of Industrial Science, The University of Tokyo,

4-6-1 Komaba, Meguro-ku Tokyo 153-8505, Japan

Fax: 81-03-5452-6341, e-mail: daichi@iis.u-tokyo.ac.jp

\*National Institute of Advanced Industrial Science and Technology,

1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

The composites of amorphous V<sub>2</sub>O<sub>5</sub> and carbon were prepared by mixing V<sub>2</sub>O<sub>5</sub> sol and carbon powder homogeneously using a surfactant. Magnesium intercalation properties into the V<sub>2</sub>O<sub>5</sub>/carbon composite electrode at relatively rapid insertion rate were examined with cyclic voltammetry and galvanostatic charge-discharge measurements using electrolyte solution of Mg(ClO<sub>4</sub>)<sub>2</sub>/acetonitrile. A composite with V<sub>2</sub>O<sub>5</sub>/carbon ratio of 0.33 in weight showed a high discharge capacity, 245 mAhg<sup>-1</sup> (based on V<sub>2</sub>O<sub>5</sub> weight) at a current density of 0.5 Ag<sup>-1</sup>. The decrease in capacity with increase in current density was slow. As a result the capacity held to be 120 mAhg<sup>-1</sup> even at a high current density of 20 Ag<sup>-1</sup>. The V<sub>2</sub>O<sub>5</sub>/carbon composite was found to be a promising candidate for the cathode material of magnesium supercapacitor.

Key words: vanadium pentoxide, magnesium insertion, high rate, supercapacitor

### 1. INTRODUCTION

Developments of rechargeable batteries, which have higher energy density than conventional lead-acid and nickel-cadmium systems are carried out eagerly all over the world. Most of them concern lithium rechargeable batteries. Magnesium, on the other hand, is also attractive anode material for the reasons that it has relatively low equivalent weight and negative standard potential. Moreover, magnesium is a low cost material, safe to handle, environmental friendly, and plentiful in natural resources. Nevertheless, it was difficult to use magnesium metal as anode in the commonly used organic electrolyte because of the growth of passivating surface film, which obstructs electrochemical reaction [1]. To this point, D. Aurbach *et al.* proved that organohaloaluminate salt allowed Mg to dissolve and deposit reversibly [2]. That has drawn more attention to Mg rechargeable batteries than before.

The requirements for cathode material of Mg batteries are strict since it is difficult for divalent magnesium ion to intercalate and diffuse in solid state material compared to monovalent lithium ion. In various kinds of candidates for cathode materials of magnesium battery, it was reported that vanadium pentoxide was promising material [3]. P. Novák *et al.* reported that reversible Mg<sup>2+</sup> intercalated in orthorhombic V<sub>2</sub>O<sub>5</sub> at room temperature [4]. They carried out cyclic voltammetry at a very slow rate of 0.02 - 0.05 mV/s in 1M Mg(ClO<sub>4</sub>)<sub>2</sub> + 1M H<sub>2</sub>O/acetonitrile, and showed that the amount of inserted magnesium was 0.58 moles per 1 mol V<sub>2</sub>O<sub>5</sub> at 1st discharge process, then that decreased to be about half at fifth discharge. D-B. Le *et al.*, on the other hand, reported magnesium insertion into V<sub>2</sub>O<sub>5</sub> aerogel prepared by supercritical drying [5]. They described that two moles of magnesium per 1 mol V<sub>2</sub>O<sub>5</sub> could be inserted chemically using dibutylmagnesium. They also performed Mg insertion electrochemically using 0.1 M

Mg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>/propylenecarbonate as a electrolyte. According to them, maximum content of Mg was less than Mg<sub>0.6</sub>V<sub>2</sub>O<sub>5</sub>.

Previously we reported that a kind of vanadium pentoxide xerogel obtained by a reaction of metallic vanadium with hydrogen peroxide [6] intercalates lithium electrochemically up to  $x = 2.55$  in terms of Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> and that charge after discharge proceeded reversibly [7]. Recently we fabricated a V<sub>2</sub>O<sub>5</sub>/carbon composite which was obtained by adding acetylene black in the V<sub>2</sub>O<sub>5</sub> sol with acetone, and demonstrated that a cathode formed by loading that composite on a nickel foamed metal as a current collector could be discharged under 150 C-rate at a relatively small sacrifice of capacity [8]. The value of 150 C corresponds to 54 A/g-cathode. Consequently, a V<sub>2</sub>O<sub>5</sub>/carbon composite was confirmed to work with a high power and high capacity.

This kind of devices with high power density and high capacity are sometimes called supercapacitors, which attract much attention especially nowadays for complementary power sources of hybrid electric vehicles (HEV). The main source of HEV can be chosen among fuel cells or rechargeable battery. Supercapacitors can supply a vehicle with required power during acceleration and also store energy in deceleration stage. The supercapacitor usually means electrical double layer capacitor (EDLC) in which charge is stored in the electric double layer between an electrolyte and an electrode. As an electrode, carbon have been widely studied. Although EDLC has high power density, its capacity is not high enough for electric vehicle in the present. Another approach for the supercapacitor is to improve the specific power of secondary battery like Li-ion cells, they originally have much higher specific energy than EDLC. The development of supercapacitors using V<sub>2</sub>O<sub>5</sub>/carbon

composites mentioned above is one of the latter approaches. Other ways to improve the power density of  $V_2O_5$  was also reported previously. Passerini et al. proposed to use vanadium oxide aerogel with high surface area [9] and F Coustier et al. reported the improvement of electric conductivity by doping of Ag or Cu [10].

As mentioned above, the composites of  $V_2O_5$ /carbon can intercalate  $Li^+$  rapidly and  $V_2O_5$  can also intercalate  $Mg^{2+}$ . These properties of  $V_2O_5$  interest us in high rate Mg intercalation into  $V_2O_5$ /carbon composites.

The purpose of this study is to evaluate the supercapacitor properties based on the pseudo-capacity of divalent  $Mg^{2+}$  intercalation. In this paper, we attempted magnesium insertion into  $V_2O_5$ /carbon composites and evaluated their performance at high current density.

## 2. EXPERIMENTAL

### 2.1. Preparation of $V_2O_5$ sol

A  $V_2O_5$  sol was prepared by the reaction of hydrogen peroxide and metallic vanadium powder [6] as follows. Metallic vanadium powder (325 mesh) was dissolved in an ice-cooled 30 wt%  $H_2O_2$ , to yield a bright reddish brown solution. It was quickly filtrated and kept at room temperature. After a vigorous reaction which was accompanied with decomposition of excess  $H_2O_2$ , the solution turned into a dark brown sol with a considerable viscosity.

### 2.2 Preparation of composite electrodes

The sol, as prepared above, pure water and acetone were mixed at a volume fraction of 1:1:1. Then carbon powder (carbon/ $V_2O_5$  ratio was 100 - 400 % in weight) was added to the solution mixture and stirred vigorously. In this study, acetylene black (Tokyo Denkikagaku Kogyo, nominal specific surface area is  $61 \text{ m}^2/\text{g}$ ) was employed as a carbon according to Kudo *et al.* [8]. After stirring for 1 h, a homogeneous suspension of a  $V_2O_5$ /carbon composite was obtained. In this fabrication manner, acetone worked as a surfactant and was essential for homogeneous suspension.

A current collector substrate was soaked in the suspension. A macroporous nickel foamed metal (Sumitomo Denka) with an average pore diameter of  $20 \mu\text{m}$  was used as current collector. After soaking, that was dried at room temperature for 12 h and heat-treated at  $120^\circ\text{C}$  for 5.

Figure 1 shows a schematic image of the composite particles at the carbon/ $V_2O_5$  ratio of 1.4. That was based on the observation of SEM [8]. Nickel substrate was covered with carbon particle. Carbon particles were coated with  $V_2O_5$  gel of 100 nm or less in thickness and dispersed on the nickel substrate.

### 2.3. Electrochemical measurements

Electrochemical measurements were performed using sealed three-electrode glass cells. These cells consisted of two bottles and designed so that one bottle should connect to the other excessively thin glass tube whose tip located in the vicinity of a working electrode. As an electrolyte, 1 mol/l magnesium perchlorate (Kanto Kagaku) dissolved in acetonitrile was used. The electrolyte solution was thought to contain water at

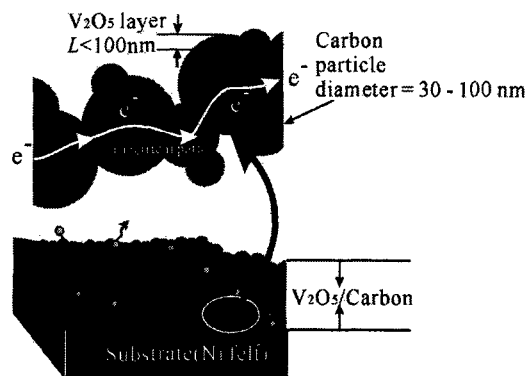


Fig. 1. Schematic image of  $V_2O_5$ /carbon composite electrode based on the SEM observations.

certain degree because the hygroscopic electrolyte  $Mg(ClO_4)_2$  was not dried prior to dissolution. We took it into considering that the proper amount of water in  $Mg(ClO_4)_2$ /acetonitrile was known to promote the Mg insertion property of  $V_2O_5$  [4]. As a counter electrode, magnesium ribbon was employed. As a reference electrode, we used a silver wire which was put into a solution of 0.01 mol/l  $AgNO_3$  and 0.1 mol/l tetrabutyl ammonium perchlorate in acetonitrile. This solution was charged in an additional glass tube with the Vycor membrane glass. This tube was dipped into one bottle which  $Mg(ClO_4)_2$ /acetonitrile was put in. This bottle was connected with a capillary to the other as stated above. To minimize the effect of IR drop associated with the electrolyte resistance, the tip of a capillary was placed as close as possible to the sample electrode.

Cyclic voltammetry and galvanostatic charge/discharge tests were carried out at room temperature using automatic polarization system (Hokuto Denko, HZ-3000). The cutoff voltages were set at  $-0.15 \text{ V}$  and  $-0.95 \text{ V}$  vs.  $Ag/Ag^+$ . The magnesium content was determined by inductively coupled plasma atomic emission spectroscopy.

## 3. RESULTS AND DISCUSSION

### 3.1 Cyclic Voltammetry

Figure 2 shows a typical cyclic voltammogram of a composite electrode.  $V_2O_5$  : carbon was 1 : 1.3 and sweep rate was  $1 \text{ mVs}^{-1}$ . At the first cathodic sweep, a maximum reduction current was observed at about  $-0.85 \text{ V}$  vs.  $Ag/Ag^+$ . This is consistent with the result of  $V_2O_5$  polycrystals [4]. In following anodic process, there was not clear peak and coulombic capacity decreased. After 2nd cycle, relatively good reversible behavior was observed. However, peak potential in cathodic process changed to  $-0.75 \text{ V}$ . It is assumed that the irreversible change of the structure occurred at the 1st insertion of magnesium.

After the first cathodic sweep to  $-0.95 \text{ V}$ , the molar ratio of inserted Mg to  $V_2O_5$  was found to be 0.85, which was about 68 % of the integration of current. Thus the coulombic efficiency was 0.68. This means that some side reactions occurred on the first cathodic process. At the following anodic scan up to  $-0.15 \text{ V}$ , the composition changed into  $Mg_{0.46}V_2O_5$ . In this process, change in magnesium content agreed well with the

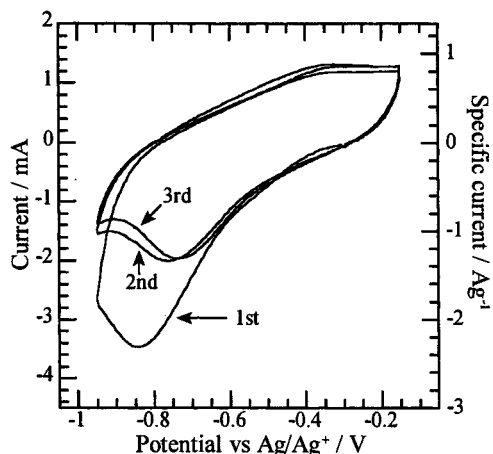


Fig. 2. Cyclic voltammogram of  $V_2O_5$ /carbon composite ( $V_2O_5$  : carbon = 1 : 1.3) at the scanning rate of 1mV/s.

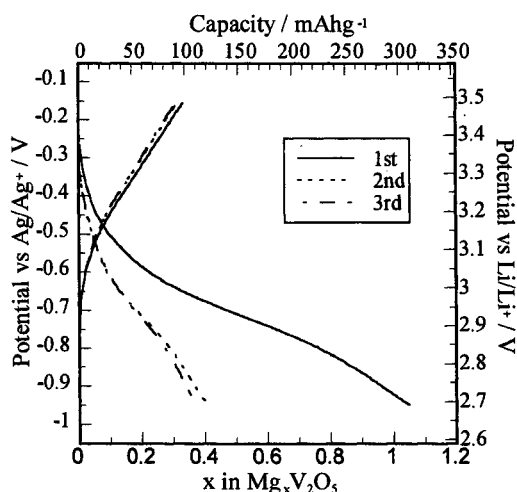


Fig. 3. Charge/discharge curves of  $V_2O_5$ /carbon composite ( $V_2O_5$  : carbon = 1 : 1.3) at the current density of 1.0 A/g.

integration of current. After 2nd cycle, Mg was inserted and extracted reversibly.

The amount of inserted magnesium in 1st discharge was larger than 0.58 for crystalline  $V_2O_5$  reported by P. Novák *et al* [4] though the sweep rate was 50 times as high as that in ref [4]. This shows that these composite electrodes could intercalate magnesium rapidly as well as lithium, compared to conventional  $V_2O_5$  electrodes and probably many other intercalation electrodes.

### 3.2 Charge/discharge tests

Figure 3 shows the result of galvanostatic charge/discharge test for the sample with  $V_2O_5$  : carbon = 1 : 1.3 under 1  $Ag^{-1}$  of current density. The value of current density, hereafter, is expressed referred to unit mass of  $V_2O_5$ , unless otherwise mentioned. The right ordinate scale gives potential based on  $Li/Li^+$ . The potential range where Mg inserted in  $V_2O_5$  was from  $-0.15$  to  $-0.95$  V vs.  $Ag/Ag^+$ , which is corresponding to 3.5 to 2.7 V vs.  $Li/Li^+$  and similar to that for Li insertion.

That similarity implies that pentavalent vanadium ions were reduced at similar potential for both intercalations. The behavior of charge/discharge was well consistent with the result of CV in the respects that the first discharge process consumed more charge than the following process and that after first charge both discharge and charge processes showed good reproducibility. At the 1st discharge process, high capacity over  $300 \text{ mAhg}^{-1}$  was observed. This value must include the capacity due to some irreversible reactions that were not clarified as mentioned above. Even so, after second cycle, the capacity remained about  $100 \text{ mAhg}^{-1}$ . These natures mean that this composite electrode can function as a cathode of Mg secondary batteries.

### 3.3 Evaluation of high-rate performance

With a view to obtaining high specific capacity, carbon ratio of the composites needs to be optimized because wasteful carbon lowers that. Figure 4 shows the

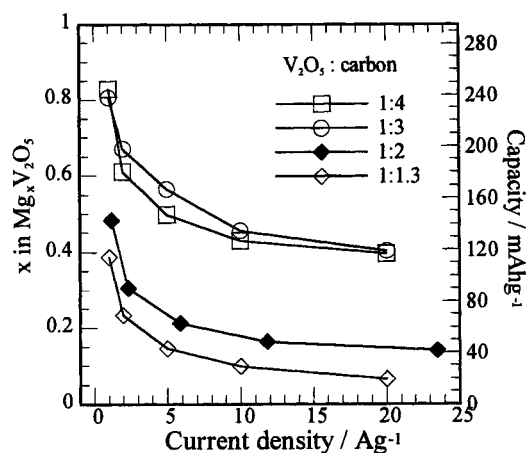


Fig. 4. Capacity vs. current density for the composites with various  $V_2O_5$ /carbon ratios.

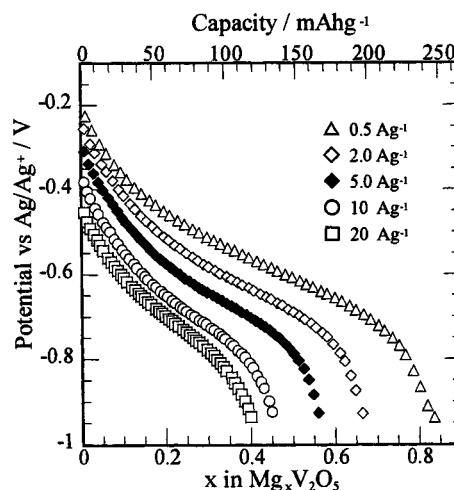


Fig. 5. Discharge curves of  $V_2O_5$ /carbon composite ( $V_2O_5$  : carbon = 1 : 3) at various current densities between 0.5 and 20 A/g.

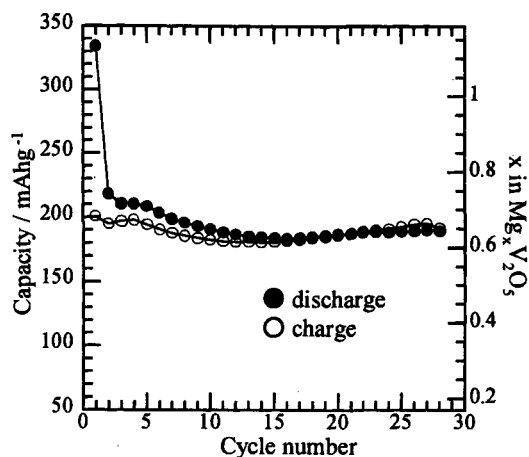


Fig.6. Cycle performance of  $V_2O_5$ /carbon composite ( $V_2O_5$  : carbon = 1 : 3) at a current density of 2.0 A/g.

relationship between galvanostatic discharge capacity and current density for the samples with various carbon ratios. For the discharge capacities in Fig. 4, we adopt ones after second cycle. The capacity increased with the carbon ratio in small ratio region, but it leveled off around the  $V_2O_5$ /carbon ratio of 1 : 3. At this carbon ratio, composite electrode seemed to permit  $V_2O_5$  to intercalate the largest amount of Mg under each current density. In terms of discharge capacity of battery which is based on its weight, the carbon should be mixed in the weight ratio  $V_2O_5$  : carbon = 1 : 3.

Charge/discharge curves of the composite electrode with  $V_2O_5$  : carbon = 1 : 3 were measured in the same cell for three cycles in each current density. In Fig.5, second discharge curves in each current density are shown. A high discharge capacity, 245  $\text{mAhg}^{-1}$  was observed at a relatively low current density of 0.5  $\text{Ag}^{-1}$ . The capacity gradually decreased with increasing of current density. Nevertheless it had about 120  $\text{mAhg}^{-1}$  even at a high current density of 20  $\text{Ag}^{-1}$ . This capacity corresponds to 0.4 moles insertion of magnesium in one molar  $V_2O_5$ .

The results of cycling test performed at a current density of 2  $\text{Ag}^{-1}$  are shown in Fig.6. After 2nd cycle, fairly good reversibility and charge/discharge efficiency was observed. In addition, relatively high capacity of approximately 180  $\text{mAhg}^{-1}$  was maintained.

Based on the results of Fig. 5, the energy density and power density of the composite electrode were estimated. The weight was for the sum of  $V_2O_5$  and carbon. For cell voltage, we adopted the potentials versus  $\text{Mg}/\text{Mg}^{2+}$  provided that we choose magnesium metal as an anode. In Fig.7, this estimation is compared with those for two cathodes of lithium ion batteries. One is the same composite electrode and the other is  $\text{LiCoO}_2$ , which is a representative cathode material of Li-ion batteries. In  $V_2O_5$ /Carbon-Mg system, higher power density than  $\text{LiCoO}_2$  was obtained, though it was inferior to the result of lithium intercalation into  $V_2O_5$ /carbon composites.

#### 4. CONCLUSIONS

The high rate magnesium insertion property of  $V_2O_5$ /carbon composites was evaluated and suitable

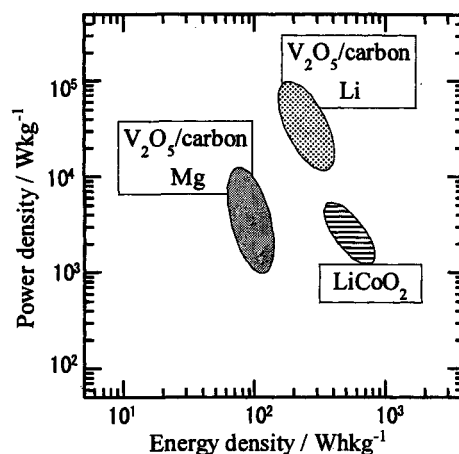


Fig.7. Energy density vs. power density based on the weight of cathode material.

carbon ratio was determined. The composites can intercalate and de-intercalate magnesium even at a high current density such as 20  $\text{Ag}^{-1}$  and hold the capacity to be 120  $\text{mAhg}^{-1}$ . Consequently, it was found that this composite is a hopeful cathode not only for magnesium ion battery but also for electrochemical supercapacitor using magnesium insertion capacity, though the further improvements are needed.

#### ACKNOWLEDGEMENTS

We would like to thank Dr. T. Watanabe, Mr. Y. Ikeda and T. Ono for helpful support in preparation of the composite electrodes.

#### REFERENCES

- [1] Z. Lu, A. Schechter, M. Moshkovich and D. Aurbach, *J. Electroanal. Chem.* **466**, 203 (1999)
- [2] D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich and E. Levi, *Nature* **407**, 724 (2000)
- [3] P. Novák, R. Imhof and O. Hass, *Electrochim. Acta*, **45**, 351 (1999)
- [4] P. Novák and J. Desilvestro, *J. Electrochem. Soc.*, **140**, 140 (1993)
- [5] D. B. Le, S. Passerini, F. Coustier, J. Guo, T. Soderstorm, B. B. Owens and W. H. Smyrl, *Chem. Mater.* **10**, 682 (1998)
- [6] M. Hibino, M. Ugaji, A. Kishimoto and T. Kudo, *Solid State Ionics*, **79**, 239 (1995)
- [7] M. Ugaji, M. Hibino and T. Kudo, *J. Electrochem. Soc.*, **142**, 3664 (1995)
- [8] T. Kudo, Y. Ikeda, T. Watanabe, M. Hibino, M. Miyayama, H. Abe and K. Kajita, *Proceedings of SSI 2001*, E-KN-01 (2001)
- [9] S. Passerini, J. J. Ressler, D. B. Le, B. B. Owens and W. H. Smyrl, *Electrochim. Acta*, **44**, 2209 (1999)
- [10] F. Coustier, J. Hill, B. B. Owens, S. Passerini and W. H. Smyrl, *J. Electrochem. Soc.*, **146**, 1355 (1999)

(Received December 20, 2001; Accepted January 31, 2002)