



# PHYSICAL CHEMISTRY 2008

## *Proceedings*

*of the 9th International Conference on Fundamental  
and Applied Aspects of Physical Chemistry*

### *Volume I*

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The Conference is dedicated to the 200th Anniversary of the University in Belgrade



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## INTERCALATION BEHAVIOR OF ELECTRODE MATERIALS OBTAINED FROM $V_2O_5 + H_2O_2$ SOLUTION

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### Abstract

$V_2O_5$  was completely dissolved in 30%  $H_2O_2$  aqueous solution, and a powdery solid product remained upon solvent evaporation was dried at 120°C. A part of the dried product was heated at 400°C up to a constant mass. By cyclic voltammetry, comparative study of  $Li^+$  and  $Mg^{2+}$  intercalation into  $V_2O_5$  and into both of its here mentioned derivatives was performed. The dissolution product dried at 120°C displayed the highest intercalation capacity amounting to 100  $mA\cdot h\cdot g^{-1}$  and 120  $mA\cdot h\cdot g^{-1}$ , in  $LiNO_3$  and  $Mg(NO_3)_2$  aqueous solutions, respectively.

### Introduction

Various vanadium oxides, especially vanadium pentoxide ( $V_2O_5$ ) are known electrode materials, applied particularly in electrochemical capacitors, electrochromic devices and Li-ion intercalation processes. Intercalation of  $Li^+$  ions into  $V_2O_5$  was widely investigated in non-aqueous solutions, and quite recently several studies have been published dealing with its electrochemical properties in aqueous solutions [1]. The main disadvantage of  $V_2O_5$ , or generally vanadates, when used as cathode material of a battery, is fast capacity fade during cyclic charging/discharging. The capacity fade was usually attributed to phase transitions during galvanostatic cycling. The way suggested to overcome this problem is either to coat the cathode material with polymer layers, or to modify its chemical composition [2].

In the present work, commercially available  $V_2O_5$  was dissolved in  $H_2O_2$ . According to previously published studies [3], precipitate recovered from such a solution may present nanoparticles or materials with highly developed surface, with improved electrochemical properties. In this work, the characterization of powdery products obtained by evaporation of  $V_2O_5 + H_2O_2$  solutions, was performed by multianalytic approach. Li-intercalation/deintercalation processes of obtained materials in aqueous solutions were investigated by means of cyclic voltammetry.

### Experimental

In the vigorous reaction, commercial  $V_2O_5$  powder (0.5g) was dissolved in 3ml of 30% hydrogen peroxide solution ( $H_2O_2$ ) and after solvent evaporation the powdery precipitate was dried at 120°C during 1h. Simultaneous TGA and DTA measurements of such dried sample indicated the further mass and phase changes

up to 350°C. Therefore, a part of the dried sample was annealed additionally at 400°C during 15 minutes.

The X-ray diffractograms (XRPD) were recorded using  $\text{CuK}_{\alpha 1,2}$  radiation in  $2\theta$  range 10-70° with the 0.05° step and 2 seconds exposition time. The scanning electron microscopy (SEM) JEOL JSM-840A was used to observe surface morphology.

Cyclovoltammetric curves were recorded at various scan rates in saturated aqueous solutions of  $\text{LiNO}_3$  and  $\text{Mg}(\text{NO}_3)_2$ . Three types of powdery materials were used to make working electrode: original  $\text{V}_2\text{O}_5$  and two powdery precipitates obtained from  $\text{V}_2\text{O}_5 + \text{H}_2\text{O}_2$  solution: that dried at 120°C, and that annealed at 400°C. To each of them, carbon black (Vulcan) and PVDF binder were added in weight ratio 60:30:10. After homogenization in N-methyl 2-pyrrolidone in ultrasonic bath, the mixture was applied on glassy carbon rod and dried under vacuum  $10^{-2}$  mbar at 140°C for 12 hours. A platinum foil was used as a counter electrode. The potentials, ranged 1 to -1 V, were measured against the saturated calomel reference electrode (SCE). Faradaic discharge capacity was calculated by coulometric analysis of cyclovoltammetric curves.

## Results and Discussion

XRPD analysis of the oxide product obtained upon  $\text{V}_2\text{O}_5$  dissolution in  $\text{H}_2\text{O}_2$  and drying at 120°C evidenced that one deals with a multicomponent amorphous mixture, while SEM images indicated its fibrous structure, Fig 1a. The width of fibers is around 1  $\mu\text{m}$ . The sample annealed at 400°C, looks like agglomerates with irregular shapes, Fig 1b.

Among the three electrode material mentioned in Experimental section, the product dried at 120°C enables the highest kinetic of both  $\text{Li}^+$  and  $\text{Mg}^{2+}$  intercalation and deintercalation. Generally for all samples, the voltammetric current increased during first few cycles and then reached a steady-state regime. For commercial  $\text{V}_2\text{O}_5$  as electrode material in Li-salt solution, average faradaic capacity was found to be 63  $\text{mAhg}^{-1}$  while the dissolution product dried at 120°C displayed faradaic capacity of roughly 100  $\text{mAhg}^{-1}$ . For Mg-salt solution, faradaic capacity of original  $\text{V}_2\text{O}_5$  was 30  $\text{mAhg}^{-1}$ , while for the dissolution product dried at 120°C the corresponding value was 120  $\text{mAhg}^{-1}$ . Faradaic capacity of the solution product annealed at 400°C was even less than that of commercial  $\text{V}_2\text{O}_5$ , as Fig. 2 shows. This capacity loss may be the

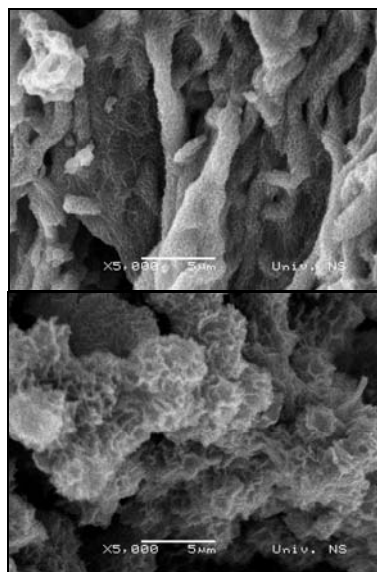
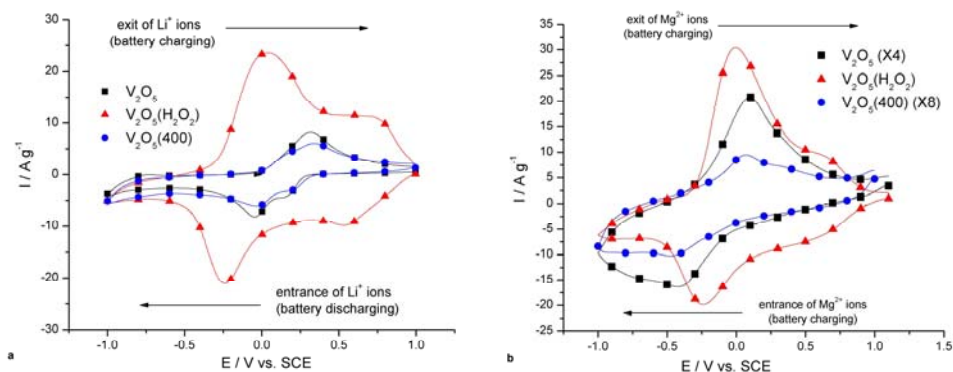


Fig. 1. SEM images of precipitate from  $\text{V}_2\text{O}_5 + \text{H}_2\text{O}_2$  solution dried at 120°C (a), and annealed at 400°C (b). The magnification was 5000.

consequence of unfavorable crystallographic ordering and particle growth during annealing procedure.



**Fig. 2.** CV curves for -▲- dissolution product 120°C -■- commercial V<sub>2</sub>O<sub>5</sub> and -●- dissolution product 400°C, in saturated aqueous solution of a) LiNO<sub>3</sub> and b) Mg(NO<sub>3</sub>)<sub>2</sub>. Scan rate was 50 mVs<sup>-1</sup>.

The performances of these materials under galvanostatic charging/discharging cycles been tested between 4.5 and 2.0 V vs Li<sup>+</sup>/Li, at current rate C/3 in organic electrolyte -1M LiClO<sub>4</sub> in propylene carbonate. After 5 cycles, the discharge capacity of the product dried at 120°C (amounting to 337 mAhg<sup>-1</sup>) was increased for 6% of initial discharge capacity (being 319 mAhg<sup>-1</sup>). Commercial V<sub>2</sub>O<sub>5</sub> as well as the annealed dissolution product displayed the capacity fade during cycling.

## Conclusion

The oxide product recovered from V<sub>2</sub>O<sub>5</sub>+H<sub>2</sub>O<sub>2</sub> solution dried at 120°C displayed most promising properties in the intercalation/deintercalation processes in aqueous electrolyte solutions of Li- and Mg- salts, and thus may be considered as potential electrode material in aqueous Li- and Mg-ion batteries.

## Acknowledgement

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## References

- [1] H. Wang, Y. Zeng, K. Huang, S. Liu, L. Chen, *Electrochimica Acta*. 2007, **52**, 5102–5107.
- [2] E. Potiron, A. Le Gal La Salle, S. Sarciaux, Y. Piffard, D. Guyomard, *Journal of Power Sources*, 1999, **81–82**, 666–669.
- [3] Z.J. Lao, K. Konstantinov, Y. Tournaire, S.H. Ng, G.X. Wang, H.K. Liu, *Journal of Power Sources*, 2006, **162**, 1451–1454.