PHYSICAL CHEMISTRY 2012

11th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Under the auspices of the
University of Belgrade

Proceedings

The Conference is dedicated to
Professor Ivan Draganić

September 24-28, 2012
Belgrade, Serbia

ISBN 978-86-82475-27-9 ***Volume*** **1**
ISBN 978-86-82475-28-6 ***Volume*** **II**

Title: PHYSICAL CHEMISTRY 2012 (Proceedings)
Editors: S. Anić and Ž. Čupić
Published by: Society of Physical Chemists of Serbia, Studenski trg 12-16, 11158, Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: "Jovan" Priting and Publishing Company; 200 Copies;
Number of pages: 6+ 497; **Format**: B5; Printing finished in September 2012.

Text and Layout: "Jovan"

200- *Coppy printing*

CONTENTS

E-09-P

ELECTROCHEMICAL BEHAVIOR OF V_2O_5 XEROGEL AND V_2O_5 XEROGEL /GRAPHITE COMPOSITE IN AQUEOUS SOLUTION

M. Medić[b], I. Stojković[a], M. Vujković[a], N. Cvijetićanin[a], S. Mentus[a,*]

[a]*University of Belgrade, Faculty of Physical Chemistry, Studentski Trg 12-16, Belgrade, Serbia*

[b] *Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, Belgrade, Serbia*

[*]*The Serbian Academy of Science and Arts, Knez Mihajlova 35, 11158, Belgrade, Serbia*

ivana@ffh.bg.ac.rs

Abstract

The V_2O_5 xerogel and V_2O_5 xerogel /graphite composite were synthesized by sol-gel method. The obtained materials were characterized by X-ray diffractometry and simultaneous thermogravimetry and differential thermal analysis. The electrochemical behaviour was investigated by galvanostatic cycling in aqueous solutions of $LiNO_3$. Better electrochemical performance was evidenced for composite V_2O_5 xerogel/graphite. Namely, the initial capacity of V_2O_5 xerogel/C was found to be 66 mAh g^{-1} against 40.4 mA h g^{-1} for V_2O_5, while capacity fade after 50 cycles was 10 % of initial capacity for V_2O_5 xerogel/ graphite, against 27% for V_2O_5.

Introduction

The rechargeable lithium-ion batteries with organic electrolytes present today the exclusively used power sources of the portable electronic devices. However, the organic electrolytes are toxic, inflammable and expensive, and there is the tendency to replace them by aqueous solutions [1]. The lithium ion batteries with aqueous solution would be more safe and cheaper. The main problem of Li-ion batteries with aqueous electrolyte is the voltage limitation arising due to the low decomposition voltage of water, and relatively poorer electrochemical characteristic of electrode materials.

In the field of lithium-ion batteries with organic and aqueous solutions, different vanadium oxides (VO_2, V_2O_5, $Li_{1+x}V_3O_8$) were investigated as electrode materials. Vanadium pentoxide (V_2O_5) in both crystalline and amorphous (xerogel) form was often studied. An amorphous (xerogel) form of V_2O_5 displayed higher capacity than the crystalline form in organic and aqueous electrolyte [2-4]. The performances during galvanostatic charging/discharging of xerogel V_2O_5 may be improved by some additives to the electrolyte solution, or by addition of nanodispersed carbon material during synthesis [3,4].

In this work, we synthesized two materials by a simple sol-gel method: xerogel V_2O_5 and composite material V_2O_5 xerogel/C, where C was finely dispersed Carbon. The intercalation/deintercalation of Li ions into both materials was investigated by galvanostatic cycling in a saturated aqueous solution of $LiNO_3$.

Experimental

Both the xerogel V_2O_5 and the V_2O_5 xerogel/graphite composite (V_2O_5/C) were synthesized in an almost identical way. In both case, the preliminary solution was obtained by dissolving crystalline V_2O_5 powder (p.a. Merck) in 10% solution of hydrogen peroxide H_2O_2 (p.a. Merck) in an amount which provided a 0.06 M solution. To obtain V_2O_5 xerogel /C composite, the natural graphite was added in the V_2O_5-H_2O_2 solution in an amount to provide mass ratio V_2O_5: C of 10 in solution V_2O_5-H_2O_2. The solution V_2O_5-H_2O_2 with and without added graphite were mixed by magnetic stirrer 24 h, then poured into a Petri cup and dried in air until the solvent evaporated. The obtained powders were dried at 200 ^oC for one hour.

The X-ray power diffraction (XRPD) data were collected using Philips PW 1050 with $CuK\alpha_{1,2}$ radiations in 10-70^o 2θ range with 0.05^o step and 2 seconds exposition time. Simultaneous TGA/DTA measurements were carried out under air flow, at a heating rate of 10 ° min^{-1} using the device TA SDT Model 2960.

The galvanostatic charge/discharge measurements were performed in a two-electrode arrangement, with V_2O_5 xerogel or composite V_2O_5 xerogel/C as active mass of the working electrode and $LiMn_2O_4$ as active component of the counter electrode, using software-controlled device Arbin BT-2042. The active material for working (or counter) electrodes was made by mixing xerogel V_2O_5 or composite V_2O_5 xerogel/C ($LiMn_2O_4$), carbon black and PVDF binder in a weight ratio 85:10:5 in N-methyl 2-pyrrolidone solvent. A drop of the suspension was deposited on stainless steel (Fe-18%Ni) plates (~6.2 cm^2). These electrodes were dried one hour at 80 °C in air and 12 hours at 140 °C under vacuum. The filter paper soaked with saturated aqueous solution $LiNO_3$ separated the electrodes. The coulombic capacity during charging/ discharging process was measured within the voltage window 0.01 to 1.3V, i.e. within the voltage window of water electrochemical decomposition.

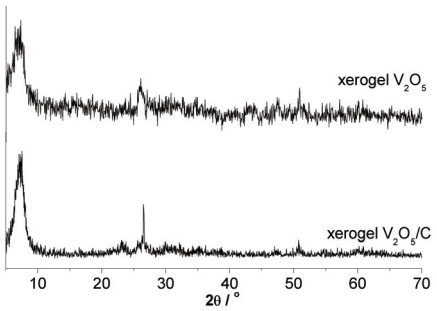

Figure 1. a) The XRD patterns of composite V_2O_5 xerogel and V_2O_5 xerogel /C composite dried at 200^{o}C.

Results and Discussion

XRPD analysis of V_2O_5 xerogel and V_2O_5 xerogel /C composite after drying at 200^{o}C evidenced amorphous structure of V_2O_5, Figure 1. The broad peak at 2θ = 25^o can be observed for composite V_2O_5/C and it belongs to graphite. The both xerogels contained 0.4 mole of H_2O per mole of oxide after heating to 200 ^oC. The amount of carbon in the synthesized material, calculated from the mass loss caused by combustion, corresponds to the initial amount of carbon in the material.

Figure 2 shows the dependence of discharge capacity (left axis) and efficiency (right axis) on the cycle number of V_2O_5 xerogel and V_2O_5 xerogel/C composite in aqueous solution of $LiNO_3$. The coulombic efficiency of both investigated materials were similar and amounted to about 96%.The V_2O_5 xerogel displayed initial capacity of 40.4 mA h g^{-1}, but its value was only 29.5 mA h g^{-1} after 50 cycles. The V_2O_5 xerogel/C composite displayed much better electro-chemical performance both before and during cycling. Its initial discharge charge capacity was 66 mAh g^{-1} and was almost constant during the first 12 cycles. After 12 cycles there appeared slight decrease and 59 mA h g^{-1} was registered after 50 cycles. A similar improvement of cycling performance was perceived for composite xerogel V_2O_5 if carbon black was added in the process of synthesis. Namely, the xerogel V_2O_5 composite /C where C is carbon black displayed initial capacity of 58.8 $mAhg^{-1}$ and after 50 cycles somewhat lower value of 43.1 $mAhg^{-1}$ was measured [4].

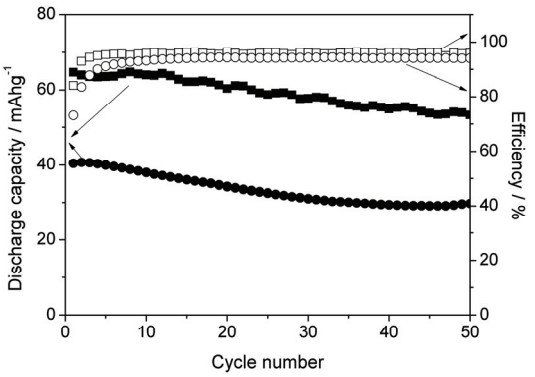

Figure 2. The discharge capacity (full symbols) and coulombic efficiency (empty symbols) of xerogel V_2O_5 (circle) and composite xerogel V_2O_5/C (square) in saturated aqueous $LiNO_3$ solution.

Conclusion

The V_2O_5 xerogel /C composite synthesized by dissolving crystalline V_2O_5 in diluted solution of H_2O_2 and adding graphite to the solution presents a promising electrode material for aqueous lithium ion batteries. Initial discharge capacity of this material was found to be 66 mAh g^{-1}, while the capacity after 50 cycles is about 90 % of its initial value.

Acknowledgement

This work was supported by Serbian Ministry of Science and Education, project No. III45014.

References

[1] N. Cvjeticanin, I. Stojkovic, M. Mitric, S. Mentus, J. Power Sources, 2007, 174, 1117-1120.
[2] D. Imamura, M. Miyayama, M. Hibino, T. Kudo, J. Electrochem. Soc,. 2003, 150, A753.
[3] I. B. Stojković, N. D. Cvjetićanin, S. V. Mentus, Electrochem. Commun., 2010, 12, 371-373.
[4] I. Stojkovic, N. Cvijeticanin, S. Mentus, Russ. J. Phys. Chem. A, 2011, 85, 2344-2348.

CIP Volume I

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

544(082)
621.35(082)
66.017/.018(082)

MEĐUNARODNA konferencija iz fundamentalne i primenjene fizičke hemije (11 ; 2012 ; Beograd)
Physical Chemistry 2012 : proceedings. #Vol. #1 / 11th International Conference on Fundamental and Applied Aspects of Physical Chemistry, September 24-28, 2012, Belgrade ; [editors S.[Slobodan] Anić and Ž.[Željko] Čupić ; organized by Society of Physical Chemists of Serbia ... et al.]. - Belgrade : Society of Physical Chemists of Serbia, 2012 (Belgrade : Jovan). - VI, 498 str. : ilustr. ; 24 cm

"The Conference is dedicated to Professor Ivan Draganić" --> nasl. str. - Tiraž 200. - Bibliografija uz svaki rad.

ISBN 978-86-82475-27-9
1. Društvo fizikohemičara Srbije (Beograd)
a) Физичка хемија - Зборници b) Електрохемијско инжењерство - Зборници c) Наука о материјалима - Зборници
COBISS.SR-ID 193432332

CIP Volime II

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

544(082)
621.35(082)
66.017/.018(082)

MEĐUNARODNA konferencija iz fundamentalne i primenjene fizičke hemije (11 ; 2012 ; Beograd)
Physical Chemistry 2012 : proceedings. #Vol. #2 / 11th International Conference on Fundamental and Applied Aspects of Physical Chemistry, September 24-28, 2012, Belgrade ; [editors S.[Slobodan] Anić and Ž.[Željko] Čupić ; organized by Society of Physical Chemists of Serbia ... et al.]. - Belgrade : Society of Physical Chemists of Serbia, 2012 (Belgrade : Jovan). - VI str., 499-782 str. : ilustr. ; 24 cm

"The Conference is dedicated to Professor Ivan Draganić" --> nasl. str. - Tiraž 200. - Bibliografija uz svaki rad. - Registar.

ISBN 978-86-82475-28-6
1. Društvo fizikohemičara Srbije (Beograd)
a) Физичка хемија - Зборници b) Електрохемијско инжењерство - Зборници c) Наука о материјалима - Зборници
COBISS.SR-ID 193433356