



PHYSICAL CHEMISTRY 2018

14th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Proceedings
Volume I

September 24-28, 2018
Belgrade, Serbia

ISBN 978-86-82475-36-1

Title: Physical Chemistry 2018 (Proceedings)

Editors: Željko Čupić and Slobodan Anić

Published by: Society of Physical Chemists of Serbia, Studentski 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", <Printing and Publishing Company, 200 Copies

Number of pages: 550+6, Format B5, printing finished in September 2018

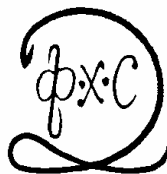
Text and Layout: "Jovan"

Neither this book nor any part may be reproduced or transmitted in any form or by any means, including photocopying, or by any information storage and retrieval system, without permission in writing from the publisher.

200 - *Copy printing*

CONTENT

<i>Volume I</i>	
<i>Organizer</i>	IV
<i>Comittes</i>	V
<i>Sponsors</i>	VI
<i>Plenary Lecture</i>	1
<i>Chemical Thermodynamics</i>	57
<i>Spectroscopy, Molecular Structure, Physical Chemistry of Plasma</i>	71
<i>Kinetics, Catalysis</i>	157
<i>Nonlinear Dynamics, Oscillatory Reactions, Chaos</i>	253
<i>Electrochemistry</i>	361
<i>Biophysical Chemistry, EPR investigations of biosystems,</i>	419
<i>Photochemistry, Radiation Chemistry</i>	



PHYSICAL CHEMISTRY 2018

*14th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry*

Organized by

*The Society of Physical Chemists of
Serbia*

in co-operation with

Institute of Catalysis Bulgarian Academy of Sciences

and

*Boriskov Institute of Catalysis Siberian Branch of
Russian Academy of Sciences*

and

University of Belgrade, Serbia:

Faculty of Physical Chemistry

Institute of Chemistry, Technology and Metallurgy

Vinča Institute of Nuclear Sciences

Faculty of Pharmacy

Institute of General and Physical Chemistry, Belgrade, Serbia

Organizing Committee

Chairman: S. Anić (Serbia)

Vice-chairmans: M. Gabrovska (Bulgaria)
A. A. Vedyagin (Russia)
S. N. Blagojević (Serbia)

Members: N. Cvjetičanin (Serbia), S. M. Blagojević (Serbia), M. Daković (Serbia), J. Dimitrić-Marković (Serbia), T. Grozdić (Serbia), Lj. Ignjatović (Serbia), D. Jovanović (Serbia), J. Jovanović (Serbia), M. Kuzmanović (Serbia), D. Marković (Serbia), B. Milosavljević (USA), M. Mojović (Serbia), N. Ostrovski (Serbia), N. Pejić (Serbia), M. Petković (Serbia), A. Popović-Bjelić (Serbia), B. Simonović (Serbia), D. Stanisavljev (Serbia), M. Stanković (Serbia), Z. Šaponjić (Serbia), B. Šljukić (Serbia), G. Tasić (Serbia), S. Veličković (Serbia), N. Vukelić (Serbia)

Scientific Committee

Chairman: Ž. Čupić (Serbia)
Vice-chairmans: V. Bukhtiyarov (Russia)
S. Todorova (Bulgaria)
B. Adnađević (Serbia)

Members: S. Anić (Serbia), A. Antić-Jovanović (Serbia), D. J. Biswas (India), R. Cervellati (Italy), G. Ćirić-Marjanović (Serbia), V. Dondur (Serbia), S. D. Furrow (USA), A. Goldbeter (Belgium), R. Jerala (Slovenia), M. Jeremić (Serbia), A. Jovović (Serbia), Y. Kalvachev (Bulgaria), E. Kiš (Serbia), Lj. Kolar-Anić (Serbia), U. Kortz (Germany), T. Kowalska (Poljska), V. Kuntić (Serbia), G. Lente (Hungary), Z. Marković (Serbia), S. Mentus (Serbia), K. Novaković (UK), B. Novakovski (Poljska), S. Otto (Netherlands), V. Parmon (Russia), R. Pascal (USA), M. Perić (Serbia), M. Plavšić (Serbia), J. Savović (Serbia), G. Schmitz (Belgium), I. Schreiber (Czech), L. Schreiberova (Czech), H. W. Siesler (Germany), E. M. Barbosa Souto (Portugal), N. Stepanov (Russia), E. Szabó (Slovakia), R. Tomovska (Spain), Á. Tóth (Hungary), M. Trtica (Serbia), V. Vasić (Serbia), D. Veselinović (Serbia), D. Vučković (Canada), V. Vukojević (Sweden), P. Walde (Switzerland)

Local Executive Committee

Chairman: S.N. Blagojević
Vice-chairmans: A. Ivanović-Šašić
A. Stanojević

Members: M. Ajduković, I. N. Bujanja, A. Dobrota, J. Dostanić, D. Dimić, A. Ignjatović, S. Jovanović, Z. Jovanović, A. Jović, N. Jović-Jovičić, D. Lončarević, M. Kragović, J. Krstić, S. Maćešić, J. Maksimović, S. Marinović, V. Marković, D. Milenković, M. Milovanović, T. Mudrinić, B. Nedić, M. Pagnacco, A. Pavićević, N. Potkonjak, D. Ranković, M. Ristić, B. Stanković, K. Stevanović, M. Stević, A. Stoilković

SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL PROPERTIES OF $\text{Na}_{0.44}\text{MnO}_2$ IN NaNO_3 AND LiNO_3 AQUEOUS SOLUTION

A. Gezović¹, M. Vujković¹, D. Jugović², I. Janković-Častvan³, I. Stojković Simatović^{1,*} and S. Mentus^{1,4}

¹University of Belgrade, Faculty of Physical Chemistry, Belgrade, Serbia.
(ivana@ffh.bg.ac.rs)

²Institute of Technical Sciences of SASA, Belgrade, Serbia.

³University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia

⁴Serbian Academy of Sciences and Arts, Belgrade, Serbia

ABSTRACT

$\text{Na}_{0.44}\text{MnO}_2$ synthesized by glycine-nitrate method (GNM) was described in this paper and it was characterized by X-ray powder diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM). Electrochemical performances of $\text{Na}_{0.44}\text{MnO}_2$ were studied by cycling voltammetry (CV) at various scan rates in NaNO_3 and LiNO_3 aqueous solutions in order to compare the intercalation/deintercalation kinetics of Li^+ and Na^+ ions. The initial discharge capacity was found to be 27.1 and 27.44 in the aqueous solution of NaNO_3 and LiNO_3 , respectively, and after 30 cycles its values increased for 12% in both electrolytes.

INTRODUCTION

The rechargeable batteries are seen as one of the most promising system for energy conversion and storage. Lithium-ion batteries (LIBs) are the most investigate type of rechargeable battery, due to its specific energy and specific power, high energy density storage, small weight and long life time [1]. In recent years, the development of the sodium-ion batteries (SIBs) has become more attractive, owing to the low cost and natural abundance of sodium, as well as the physicochemical similarity with lithium. The working principle of SIBs is identical to LIBs. One of the main problems of SIBs is the larger radius of Na-ion than of Li-ion, which could cause more difficult intercalation compared to Li-ion [2]. Until now investigated LIBs and SIBs use highly toxic and flammable organic solvents which have low ionic conductivity and high price. Aqueous LIBs and SIBs have a series of advantages: they do not contain flammable organic electrolytes, the ionic conductivities of the aqueous electrolyte is about two orders of magnitude higher than in nonaqueous electrolyte and the electrolyte salt and solvent are

cheaper. Manganese oxides, vanadium oxide or phosphates are used as electrode materials (cathodic and anodic) in both types of batteries. Li–Mn–O or Na–Mn–O systems with tunnel or layered crystal structures are the mostly used type of manganese oxides as electrode materials. $\text{Na}_{0.44}\text{MnO}_2$ (NMO) have been synthesized by different methods such as hydrothermal process, thermo-chemical conversion process, polymer-pyrolysis process, molten salt technique, electrostatic spinning method, spray pyrolysis process and spray drying process [3]. In this work NMO was synthesized by glycine-nitrate method (GNM), which, according to the literature, has not been used for synthesis of this material so far.

EXPERIMENTAL

NaNO_3 and $\text{Mn}(\text{NO}_3)_2$ aqueous solutions were mixed in ratio corresponding to a stoichiometric ratio of Na/Mn in NMO. The glycine was added to the mixture with molar ratio of glycine-to-nitrate 1.2. The resulting precursor solution was placed in a glass beaker and heated in an oven until spontaneous ignition occurred. The obtained powder was heated in the air at $900\text{ }^\circ\text{C}$ for 4 h.

The structure of synthesized powder was characterized by X-ray diffraction (XRD) and XRD pattern was recorded at Philips PW-1050 over a 2θ range $10\text{--}70^\circ$ with a step of 0.05° and a counting time of 5 s. The morphology of the synthesized powder was analyzed by FE-SEM (TESCAN, MIRA 3 XMU) at 20 kV. The electrochemical behavior of NMO was investigated by cyclic voltammetry (CV) at various scan rates, in both NaNO_3 and LiNO_3 aqueous solutions using Gamry PCI4/300 Potentiostat/Galvanostat/ZR

A in three-electrode cell. A platinum foil was used as a counter electrode, saturated calomel electrode (SCE) was used as a reference electrode and the working electrode was made of NMO powder (85%), carbon black (10%) and polyvinylidene fluoride (5%) in N-methyl-2-pyrrolidone as solvent. The suspension was homogenized in an ultrasonic bath to form homogeneous slurry and afterwards transferred on

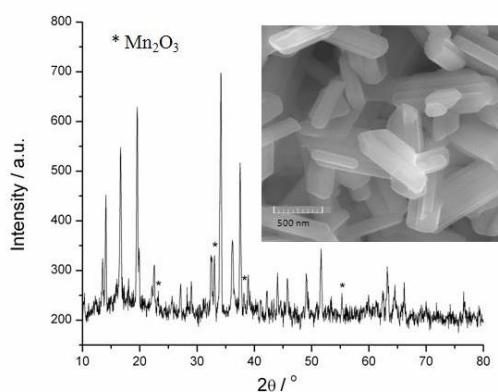


Figure 1. XRD pattern and FE-SEM image of $\text{Na}_{0.44}\text{MnO}_2$. The asterisk shows the positions of Mn_2O_3 reflections.

glassy carbon rod and dried under vacuum 10-2 mbar at 140°C for 4h.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of the synthesized material. The sharp diffraction peaks indicated that the product was well-crystallized and was identified as orthorhombic structured of $\text{Na}_{0.44}\text{MnO}_2$ with *Pbam* space group (JCPDS No.27-0750). A minor amount of impurities was detected and identified as Mn_2O_3 (JCPDS No.41-1442) [3]. The FE-SEM images of NMO indicated that the powder consisted of uniform rod-like particles and the average width and length of particles were found to be ~80 nm and ~800 nm, respectively, Fig 1.

Cyclic voltammograms of NMO recorded in NaNO_3 and LiNO_3 aqueous solutions, by high polarization scan rates from 20 to 400 mV s^{-1} within the voltage range -1.30 to 1.35 V vs. SCE, are shown on Fig. 2. For both solutions, the shape of CV's and peaks position were similar for all rates which means that process of intercalation/deintercalation of Li^+ and Na^+ are reversible and synthesized material can be used in lithium and sodium batteries. In NaNO_3 electrolyte at a polarization rate of 20 mVs^{-1} , NMO showed three anodic peaks at the potential 0.005, 0.723 and 1.168 V and two cathodic peaks at the potentials of 0.4 and - 0.32 V vs. SCE. In the case of LiNO_3 as an electrolyte, the three anodic peaks were present at the potential 0.116, 0.649 and 1.206 V while two cathodic peaks were at the potential 0.729 and - 0.242 V vs. SCE.

The initial discharge capacity of NMO in NaNO_3 and LiNO_3 aqueous solution at the polarization rate of 20 mV s^{-1} is 27.1 and 27.4 mAh g^{-1} while

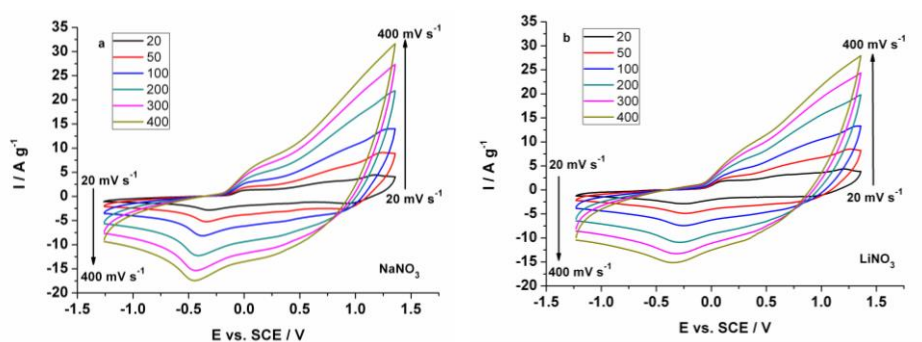


Figure 2. CV's of $\text{Na}_{0.44}\text{MnO}_2$ in aqueous solution of a) NaNO_3 and b) LiNO_3 at scan rate of 20, 50, 100, 200, 300 and 400 mVs^{-1} .

initial charge capacity is 30.6 and 30.5 mAh g⁻¹, respectively. The discharge capacity of NMO in NaNO₃ and LiNO₃ electrolytes, after 30 cycles, at the same polarization rate, was increased to values 51.1 and 53.3 mAh g⁻¹, while charge capacity was 50.8 and 53.9 mAh g⁻¹, respectively. With the increase in polarization rates from 20 to 400 mVs⁻¹, the discharge capacity decreases to 14.6 and 13.3 mAh g⁻¹, and charge capacity decreases to 14.8 and 12.8 mAh g⁻¹, in both NaNO₃ and LiNO₃, respectively.

CONCLUSION

In summary, Na_{0.44}MnO₂ was successfully synthesized by glycine-nitrate method and the powder consisted of uniform rod-like particles. The intercalation/deintercalation of lithium and sodium ions in synthesized material were reversible in NaNO₃ and LiNO₃ aqueous electrolyte which indicated that Na_{0.44}MnO₂ synthesized by glycine-nitrate method can be used as the positive material in lithium and sodium aqueous batteries.

Acknowledgement

This work was supported by the Ministry of Sciences and Environmental Protection of Serbia (Project III 45014) and SANU (Electrocatalysis in the contemporary process of energy conversion).

REFERENCES

- [1] E.C. Evarts, Nature Vol 526, pp 93-95, 2015.
- [2] A. M. Skundin, T. L. Kulova and A. B. Yaroslavtsev, Russian Journal of Electrochemistry Vol 54, pp. 131–174, 2018.
- [3] M. Vujković, B. Sljukić, I. Stojković-Simatović, M. Mitrić, C. Sequeira, S. Mentus, Electrochim. Acta Vol. 147, pp. 167, 2014.
- [4] X. Zhou, R. K. Guduru, P. Mohantya, J. Mater. Chem. A Vol 1, pp 2757-2761, 2013.