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Na_{0.44}MnO₂ as a cathode material for aqueous sodium-ion batteries

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The application of rechargeable batteries is growing significantly and it became the most important field for large-scale electric energy storage. While lithium-ion batteries (LIBs) have great commercial success, due to their large energy and power density, their application was limited because of the availability of lithium and its high cost. Sodium-ion batteries (SIBs) can be a promising alternative due to the huge availability of sodium, its low price and similar intercalating electrochemistry to LIBs [1]. Among various Na-ion battery materials, low-cost and tunnel-type, Na_{0.44}MnO₂ (NMO) was regarded as one of the most promising cathode materials for sodium-ion batteries, because of its high theoretical specific capacity (122 mA h g⁻¹) and good cyclability [2]. In this work, for the synthesis of NMO powder, rapid glycine-nitrate method (GNM) was used, which, on the basis of the literature review, has not been used to synthesize this material so far.

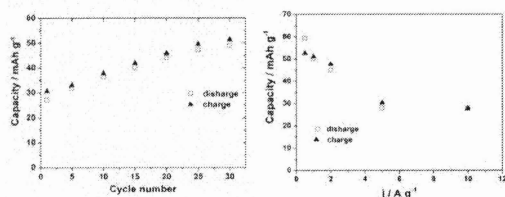


Figure 1. The discharge/charge capacity of Na_{0.44}MnO₂ vs. number of cycles (left) and current rates (right) in aqueous NaNO₃ solution.

Na_{0.44}MnO₂ as a potential cathode material for sodium-ion batteries, was synthesized by glycine-nitrate method (GNM). Powder synthesis procedure includes preparation and mixing of NaNO₃ and Mg(NO₃)₂ aqueous solutions, corresponding to a stoichiometric ratio of 0.44 for Na/Mn. 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 °C for 4 h. The structure and morphology of synthesized powder were characterized by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM). XRD patterns were recorded at Philips PW-1050 over a 2θ range 10–70° with a step of 0.05° and a counting time of 5 s. The morphology of the synthesized powder was analyzed by FESEM (TESCAN, MIRA3 XMU) at 20 kV. The electrochemical behavior of NMO was investigated by cyclic voltammetry (CV) and chronopotentiometry (CP) in NaNO₃ aqueous solution.

Electrochemical performances were tested by cyclic voltammetry and chronopotentiometry using Gamry PCI4/300 Potentiostat/ Galvanostat/ ZRA) in NaNO₃ aqueous solution. A platinum foil was used as a counter electrode, while saturated calomel electrode was used as a reference electrode. The working electrode was made of NMO powder (85%), carbon black (10%) and polyvinylidene fluoride (5%), as binder, in a certain amount of N-methyl-2-pyrrolidone, as solvent. The suspension was homogenized in an ultrasonic bath to form a homogeneous slurry and afterwards transferred on glassy carbon rod and dried under vacuum 10⁻² mbar at 140°C for 4 h. The phase structure of the product was identified as orthorhombic structured Na_{0.44}MnO₂ with *Pbam* space group (JCPDS No.27-0750). A minor amount of impurities was detected and identified as Mn₂O₃ (JCPDS No.75-1560) [3]. The average width and length of uniform rod-like particles were found to be ~80 nm and ~800 nm, respectively. CVs showed is capable of intercalating/deintercalating sodium ions in an aqueous electrolyte solution. The initial charge and discharge specific capacity, measured in aqueous solution of NaNO₃ at scan rate of 20 mV s⁻¹, amounted to 30,6 mA h g⁻¹ and 27,1 mA h g⁻¹, respectively. It increases (Fig.1) throughout charging/discharging, reaching the value of 51.4 mA h g⁻¹ and 48.9 mA h g⁻¹, after 30 cycles. CP measurements revealed that the capacity decreases with the increase of the current rates. It's discharging values were found to be 59.4 mA h g⁻¹ at 0.5 A g⁻¹ and 27.8 mA h g⁻¹ at 10 A g⁻¹ (Fig.1). Relatively high discharge capacity makes it promising cathode material for aqueous rechargeable sodium-ions batteries. This study was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia under Grant no III45014 and the Serbian Academy of Sciences and Arts through the project F-190 "Electrocatalysis in the contemporary processes of energy conversion".

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Aleksandra Gezović was born in 01.01.1995. in Nikšić, Montenegro. She received Bachelor degree (BSc) in Chemical Technology, at the Faculty of Metallurgy and Technology, University of Montenegro (2016). At the same faculty (2017), she finished Specialized Academic Studies (Sci) (course -Electrochemical processes and products) in the field of Corrosion. She enrolled in Master Academic Studies at the Faculty of Physical Chemistry, University of Belgrade (October, 2017). Current research is focused on the synthesis, characterization and investigation of electrode materials for application in batteries.

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