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Proof-of-concept study of a new type sodium-ion hybrid electrochemical capacitor with organic electrolyte

Krzysztof Wasiński*, Paulina Półrolniczak, Mariusz Walkowiak

Institute of Non-Ferrous Metals Division in Poznań, Central Laboratory of Batteries and Cells, Forteczna 12 St., 61-362 Poznań, Poland

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ABSTRACT

This paper aims to demonstrate a novel electrochemical energy storage device, a hybrid Na-ion capacitor with organic electrolyte. Sodium manganese oxide having formula $Na_{0.4}MnO_2$ has been chosen and synthesized as the most suitable battery-type positive electrode, while activated carbon (AC) has been utilized as the capacitor-type negative electrode. Due to the application of propylene carbonate based organic electrolyte, the maximum safe operating voltage of the device has been established as high as 2.7 V, giving rise to a specific capacitance of 17.4 F g^{-1}, significantly higher as compared to the analogous symmetrical EDLC measured in our laboratory based on AC electrodes in the same electrolyte.

1. Introduction

Hybrid electrochemical capacitors have recently emerged as a new class of electrochemical energy storage devices. According to the nomenclature proposed by Cericola et al. [1], hybrid capacitor is an electrochemical cell or device in which one of the electrodes (either positive or negative) relies predominantly of faradaic processes (this is referred to as "battery-type"), whereas the other electrode relies predominantly on electrostatic phenomena (and thus is referred to as "capacitor-type") [2]. Hybrid capacitors form a sub-set of asymmetric capacitors, which may be either hybrid or purely capacitive in character (and in this latter case are referred to as asymmetric electrochemical double layer capacitors (EDLC)). Among hybrid capacitors, so-called Li-ion capacitors (LIC) have already gathered a huge amount of scientific effort [3]. Na-ion capacitors (NIC), on the other hand, only just begin to attract wider attention, in close conjunction with clearly observed progress in the development of sodium insertion electrode materials for Na-ion batteries and knowledge on the associated phenomena [4–10]. As far as organic electrolyte-based devices are considered, several authors have recently claimed to have presented a hybrid Na-ion capacitor. However, under close scrutiny, only some of the described systems do in fact fulfill the conditions legitimizing the usage of the term hybrid Na-ion capacitor in a strict and widely accepted sense. In particular, systems comprising originally two sodium-free electrodes cannot be regarded as sustainable Na-ion storage devices since lack of sodium source will each time inevitably lead to the electrolyte depletion in Na^+ ions upon the device charging. None of the relevant scientific reports considers credibly the implications of this fact, including unavoidable variations in electrolyte conductivity, the cell internal resistance and feasibility of the application of significantly higher than typical initial sodium salt concentration in the electrolyte [11].

So far only very few authors proposed a reliable approach to hybrid Na-ion capacitors with non-aqueous electrolytes, mostly relying on mixed sodium-transition metal phosphates. For example, Sundaram et al. [12] studied $NaMn_{1/3}Co_{1/3}Ni_{1/3}PO_4$ as the sodium insertion positive electrode to be used in a hybrid device with carbon as the capacitor-type negative electrode. Very recently, Thangavel et al. [13] presented a similar approach, with carbon as the negative electrode and $Na_3V_2(PO_4)_3$ as the positive electrode. Sodium-manganese oxides with various stoichiometries ($Na_{0.4}MnO_2$, $Na_{3.6}Mn_9O_{18}$, $Na_{0.44}MnO_2$, $Na_{0.66}MnO_2$, $Na_{0.7}MnO_2$, and α- or β-$NaMnO_2$) have been studied as sodium insertion cathodes for Na-ion batteries but, to our knowledge, none of these have been considered as electrode for hybrid Na-ion capacitors with organic electrolytes [5,9,10,14]. The advantages of using Na_xMnO_2 as electrode material are the non-toxicity of Mn, low cost and easy synthesis methods. Also the morphology of the material can be easily controlled by reaction parameters. The rod-like

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* Corresponding author.
E-mail address: krzysztof.wasinski@claio.poznan.pl (K. Wasiński).

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morphology of crystals allows to work on higher C-rates in Na-ion capacitors.

The present work describes one of the first viable realizations of a Na-ion capacitor with organic electrolyte in a strict sense, comprising an activated carbon as negative electrode and, for the first time in this type of electrochemical storage device, $Na_{0.4}MnO_2$, as the redox-type, sodium-rich positive electrode.

2. Experimental

2.1. Positive electrode material synthesis

$Na_{0.4}MnO_2$ has been synthesized in a one-step solid state reaction route. Na_2CO_3 (Aldrich) and Mn_2O_3 (Aldrich) were mixed as received at a weight ratio of 4:10 and ball-milled for 6 h. The obtained mixture was subsequently placed in a furnace and heated in air to 800 °C. After 12 h of heat treatment the furnace was cooled down. The resulted dark-gray powder was milled again to obtain a fine powder.

2.2. Structural characterization

X-ray diffraction patterns have been obtained using X'Pert, PANalytical device with the application of CuKα radiation. Texture, morphology and particle size of the synthesized material was observed by scanning and transmission electron microscopy using Zeiss EVO 40 (SEM) and JOEL JEM 1200 EX (TEM) instruments.

2.3. Electrode preparation and cell assembly

The negative electrodes have been prepared by ball-milling a mixture consisting of 80 wt% of AC (Norit$^{\circledR}$ SX Ultra, Aldrich) with 1200 $m^2 g^{-1}$ specific surface area, 10 wt% carbon black (C65,Timcal) and 10 wt% carboxymethyl cellulose (CMC, Aldrich), followed by the addition of distillated water and mixing to obtain a homogenous slurry. The slurry has subsequently been cast onto current collectors (Al foil, Hohsen, Japan) and dried under vacuum at 105 °C for 24 h. The negative electrode mass loads typically ranged from 0.9 to 6.2 mg per square centimeter of the current collector. The positive electrodes have been prepared by mixing 70 wt% $Na_{0.4}MnO_2$, 10 wt% multi walled carbon nanotubes (Aldrich), 10 wt% carbon black (C65, Timcal) and 10 wt% poly(vinylidene fluoride-*co*-hexafluoropropylene) (Kynar-Flex, Atofina) as a polymeric binder with the addition of *N*-methylpyrrolidone (NMP, >99%, VWR). The obtained slurry was pasted on aluminum current collectors and dried at 105 °C under vacuum for 24 h. The positive electrodes mass load ranged from 0.9 to 1.12 mg per square centimeter of the current collector. Swagelok-type cells were assembled by sandwiching the electrodes with a tissue paper separator and propotionating the electrolyte being a 1 M solution of $NaClO_4$ (Aldrich) in propylene carbonate (Aldrich).

2.4. Electrochemical testing

Electrochemical measurements were carried out on multichannel electrochemical tester VMP-3 (Biologic) in two- and three-electrode Swagelock$^{\circledR}$ type cells assembled in argon filled glove box (MBraun) containing <0.5 ppm H_2O and O_2. In three-electrode cells metallic sodium served as the reference electrode. Cycling voltammetry (CV) tests were performed at the scan rates ranging from 1 to 100 mV s^{-1}. The galvanostatic charging/discharging profiles were recorded at 50–5000 mA per gram of the sum of masses of both electrodes.

Prior to the actual device electrochemical parameter determination, the optimal electrode mass balance has been established. Positive to negative electrode mass ratios have been varied from 1:1 to 1:6.

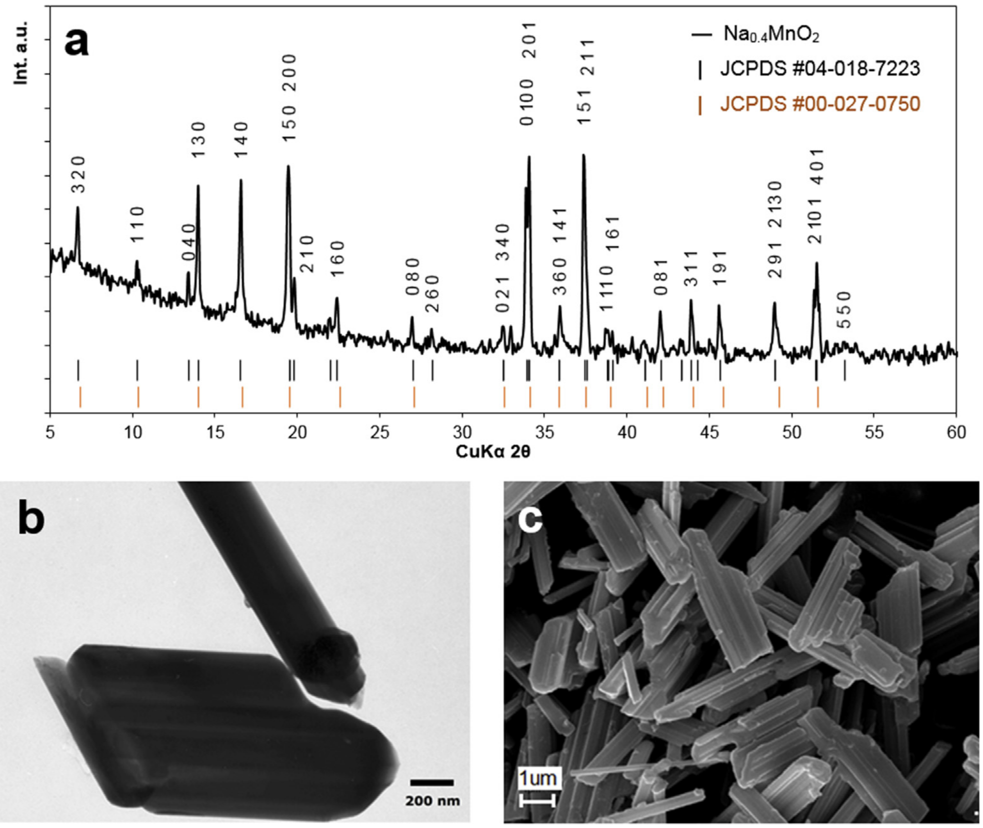

Fig. 1. Structural characterization of the synthesized positive electrode material: a) XRD pattern with marked reflections from $Na_{3.6}Mn_9O_{18}$ phase, b) SEM image, c) TEM image.