

Synthesis and Electrochemical Properties of Mesoporous α -MnO₂ for Supercapacitor Applications

P.I. Kolkovskiy, B.I. Rachiy, M.I. Kolkovskiy, B.K. Ostafiychuk, I.P. Yaremiy,
V.O. Kotsyubynsky, R.V. Ilnitsky

Vasyl Stefanyk Precarpathian National University, 57, Shevchenko St., 76018 Ivano-Frankivsk, Ukraine

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In this work, the crystal structure of α -MnO₂ has been obtained by the hydrothermal method. It was determined that the obtained material has a tunnel structure with average particle sizes of 12-15 nm. The electrochemical performances of α -MnO₂ in an aqueous solution of 30 % KOH based electrolyte have been investigated by cyclic voltammetry and galvanostatic cycling methods. At the same time, it was determined that the specific capacity of the α -MnO₂/electrolyte system decreased from 90 F/g to 55 F/g with an increase of the scan rate from 2 to 10 mV/s. Thus, the maximum values of specific capacitance about 104 F/g were obtained at 0.5 mV/s. The Coulomb efficiency of the electrochemical system is constant and independent of the cycle number under the charge/discharge process. Therefore, the total capacity of the material under investigation can be divided into the capacity of the double electric layer and the diffusion-controlled redox capacity due to the Faraday reverse redox reactions. It was determined that the contribution of pseudocapacity is 90 % of the total specific capacity. In addition, it has been determined that the α -MnO₂/KOH electrochemical system is stable under long-term cycling process.

Keywords: Manganese oxide, Pseudocapacity, Hybrid electrochemical capacitor, KOH.

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1. INTRODUCTION

Hybrid electrochemical capacitors (HECs) are of significant scientific and practical interest since they provide high power compared to batteries and have a long service life [1]. Two different mechanisms of charge accumulation are implemented in the HECs, namely the polarization of the DEL as in supercapacitors [2] and the electrochemical reaction as in batteries. HECs can fill the efficiency gap between the energy density of batteries and the high power density of conventional dielectric capacitors due to unique energy characteristics. Thus, HECs are capable of providing rapid energy storage and release [3]. Today, RuO₃ is the most promising material for HEC systems, which has high values of specific capacitance (> 700 F/g) and high cycling performance. At the same time, RuO₃ is characterized by a number of disadvantages, in particular, toxicity and high cost [4]. Thereby, it is relevant to research a number of transition metal oxides as promising materials for HEC electrodes, namely oxides of manganese, nickel, cobalt, molybdenum, etc. [5]. Materials based on manganese oxide (MnO₂) with different crystalline structures (α , β , γ , δ and λ) are promising electrode materials for HEC, as has been shown in recent investigation [6].

Various methods were used for the synthesis of MnO₂, such as precipitation, sol-gel method, reaction at room temperature, sonochemical and hydrothermal synthesis methods [7]. The advantage of using various crystalline forms of MnO₂ as HEC electrodes is a high theoretical specific capacity of ~ 1370 F/g, due to the reduction reaction ($\text{Mn}^{4+} \rightarrow \text{Mn}^{3+}$), as well as non-toxicity and low cost which made MnO₂ more attractive compared to other oxide metals such as RuO₂, IrO₂, CoOx, NiO, and Ni(OH)₂ [8].

Alpha (α) form of MnO₂ is characterized by the highest Coulomb efficiency among its other crystalline forms

according to literature data [9]. The obtained values of the electrochemical characteristics of HEC are 100-250 F/g with electrodes based on α -MnO₂. However, the obtained values are much lower than the theoretical value of the specific capacitance [10]. Probably, low values of electrical conductivity (band gap of 5.49 eV) are caused by the difficulty in electron transfer as a result of jet-forming processes, and accordingly, reduce the specific power of HEC formed on α form of MnO₂. Alternatively, a correlation was established between the electric capacity of the HEC based on α -MnO₂ and the electrical conductivity of the electrode material [11]. As a result, the low electrical conductivity of α -MnO₂ is the cause of the negative impact on the specific energy characteristics of HEC with electrodes based on them. Therefore, the addition of conductive additives is a key factor in the formation of electrodes. Materials such as silver, nanoporous carbon and carbon nanotubes, thermally expanded graphite have been widely used to create composite electrode materials MnO₂/Ag, MnO₂/C and MnO₂/CNT [12]. Thus, an increase in the electrical conductivity of the electrode material leads to an increase in the specific power of HEC formed on their basis. The charge/discharge mechanism of a HEC which was formed based on α -MnO₂ as an electrode can be described as [11]: $\text{MnO}_2 + \text{X}^+ + \text{e}^- \leftrightarrow \text{MnOOX}^+$ (where X⁺ is Li⁺, Na⁺, H⁺, K⁺ etc.). In this work, synthesis of monophasic α -MnO₂ obtained by the hydrothermal synthesis method has been investigated. Moreover, the kinetics of electrochemical charge/discharge processes in the electrode/electrolyte system has been established. As well as, the influence of the morphological characteristics of the electrode materials on the electrochemical and energy parameters of the HEC electrode materials has been established. A model of kinetic processes in an electrochemical system with electrodes based on α -MnO₂ is constructed and provides the key factor of the developed surface in the process of charge accumulation.

2. EXPERIMENTAL PROCEDURE

Monophasic mesoporous α -MnO₂ with predetermined morphology was obtained based on the redox reaction $3\text{MnCl}_2 + 2\text{KMnO}_4 + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{HCl} + 2\text{KCl}$ by hydrothermal route. As reagents for the synthesis of α -MnO₂, aqueous solutions of 0.04 M of KMnO₄, 0.06 M of MnCl₂ and 4 M cationic impurity KCl were used. Then the precursors were stirred by a magnetic stirrer for 30 min and then were placed into 150 ml Teflon autoclave. The autoclave was sealed and kept for 48 h at a temperature of 180 °C. After cooling down to room temperature, the solution was filtered, washed and dried at 120 °C for 24 h.

The phase composition and crystal structure of the obtained materials were investigated by XRD based on DRON-3M diffractometer (CuK α -radiation). Electrochemical measurements were performed based on three-electrode cells consisted of working electrode (electrode composition on pure Ni substrate of 1 cm²) reference electrode (Ag/AgCl), counter electrode (platinum wire). Electrode composition consists of 85 % active material, 10 % acetylene black and 5 % polyvinylidene fluoride mixed with *n*-methylpyrrolidone and dried at 80 °C for 3 h. 6 M KOH was used as an electrolyte. The charge/discharge measurements were done at specific current values of 0.5, 1 mA/g. Cyclic voltammetry measurements were performed at scan rate values of 1, 2, 3, 4, 5, 10, 50, 100 mV/s.

3. RESULTS AND DISCUSSION

XRD patterns of MnO₂ obtained by hydrothermal synthesis method at a temperature of 180 °C for 48 h are shown in Fig. 1. The monophasic ultrafine α form of MnO₂ phase (JCPDS no. 42-1348) with a crystal structure of Mn⁴⁺ and O²⁻ (Fig. 2) was successfully formed.

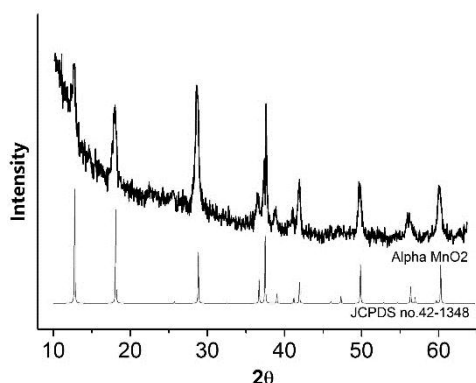


Fig. 1 – XRD patterns of the obtained sample and reference (JCPDS no. 42-1348) α -MnO₂

The average sizes of coherent scattering domains (CSD) were calculated based on Sherrer's equation. Thus, the average sizes of the CSD are 12-15 nm. As a result, the 4 M concentration of KCl ions is a key factor in the formation of the α -MnO₂ phase.

The positions in the tunneling structure of the MnO₆ octahedra are occupied by K⁺ ions interconnected by Mn–O bonds. Moreover, the channel sizes are 0.46×0.46 nm (Fig. 2).

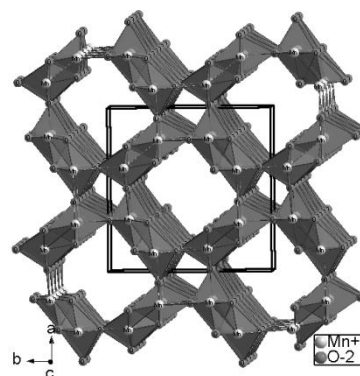


Fig. 2 – The crystal structure of α -MnO₂ view along the *c*-axis

The cyclic voltammetry method was used for investigations of the redox reactions contributing to the total capacitance of the electrode materials in the potential range from -0.2 to -0.8 compared to the Ag/AgCl reference electrode in the range of scan rates of 1-10 mV/s. CVA curves for the system analysis of α -MnO₂/electrolyte sample are asymmetric at a scan rate of 1 mV/s (Fig. 3).

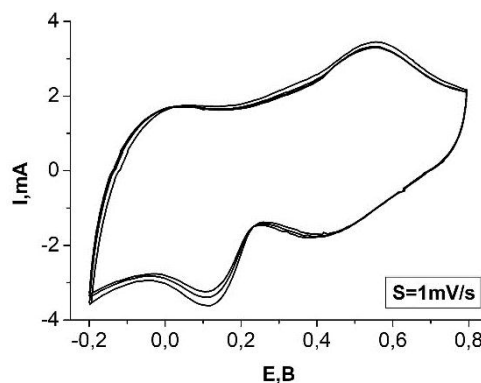


Fig. 3 – CVA curves of α -MnO₂/electrolyte system

Peaks corresponding to the maximum rate of the oxidation and reduction processes are clearly observed both on the anode and cathode branches, respectively. In this case, this confirms that the contribution to the capacity of the investigated material is provided by two mechanisms, namely, the redox reaction and the DEL charge.

It was determined that after 10, 50, and 100 scan cycles, the CVA curves retain their normal form and shape, which is evidence of the reversal of charge-discharge processes occurring in a system with electrodes based on α -MnO₂ in KOH electrolyte. According to CVA data, it was determined that after 100 cycles the specific capacity decreases by 0.5-1 %. The peaks on CVA curves at a potential range of 0.8-0.3 V are observed with an increase in the scan rate from 2 to 10 mV/s (Fig. 4). Moreover, with an increase in the scan rate, the peaks in the curves have been shifted to the region of higher potentials. This fact is the evidence of the passage in the system under investigation of fast reverse Faraday redox/reduction processes.

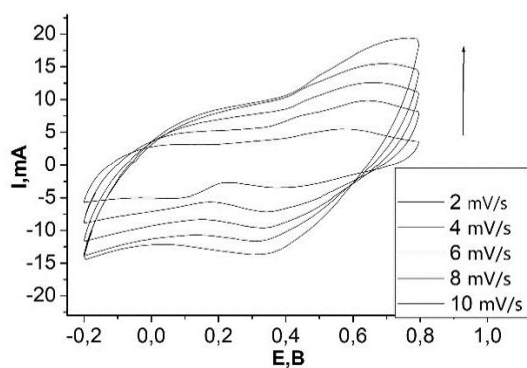


Fig. 4 – CVA curves for the α -MnO₂/electrolyte system at different scan rate

The dependence of the specific capacity of the α -MnO₂/electrolyte system on the scan rate is shown in Fig. 5.

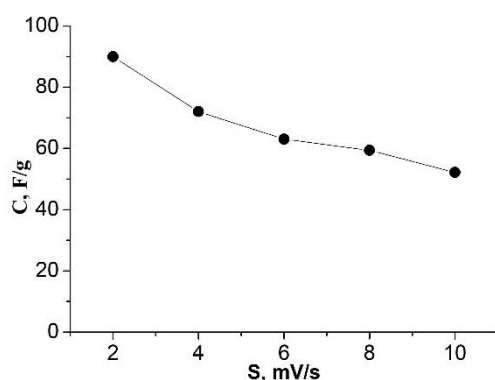


Fig. 5 – Specific capacity of the α -MnO₂/electrolyte system

The maximum values of specific capacitance about 104 F/g were obtained at 0.5 mV/s. An increase in the cycling rate has been leading to a monotonic decrease in the specific capacity of the α -MnO₂/electrolyte system. However, the stability of the system was established at a scan rate of 10 mV/s additionally, the specific capacity was obtained about 60 F/g.

The capacity of the α -MnO₂ sample is provided mainly by negative electrolyte ions (OH⁻ groups) under electrode cycling in the positive potential region. In this case, the specific capacity of the sample is decreased with increasing scan rate (Fig. 6). The total capacity of the material under investigation can be divided into the capacity of the double electric layer (C_{DEL}) and the diffusion-controlled redox capacity due to the Faraday reverse redox (C_F) $C = C_{DEL} + C_F$ reactions based on the obtained dependence of C on s [13].

Since the diffuse component of the capacity (C_F) is a function of the reaction time, it was assumed that in the kinetic model [13] the scan rate affects the total specific electrochemical capacity of the system.

Thus, the scan rate is inverse to the diffusion flow time. Therefore, the scan rate can be considered inverse to the diffusion time. As a result, the total capacity is related to the scan rate by the equation

$C = C_{s=\infty} + a/\sqrt{s}$, where a is a constant value and $C_{DEL} = C_{s=\infty}$ in the case of semi-continuous linear diffusion condition. On the one hand, the specific capacity of

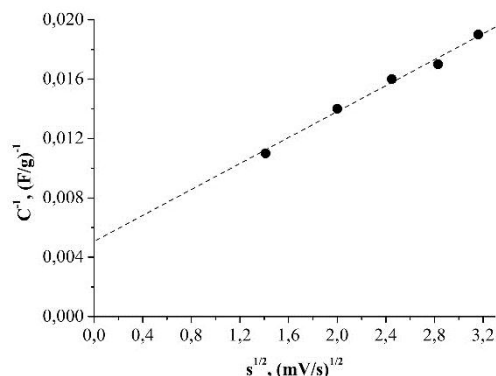


Fig. 6 – The dependence of the specific capacity C on $s^{-1/2}$

manganese oxide alpha modification is linearly dependent on $s^{-1/2}$ (Fig. 6). The specific capacity of the DEL based on investigated materials is determined due to the extrapolation of the C dependences on $s^{-1/2}$ to the Y-axis (Fig. 6) (Table 1).

At the same time, the specific capacity dependence on the scan rate can also be extrapolated to the other side to $s = 0$ by the functional dependence on s .

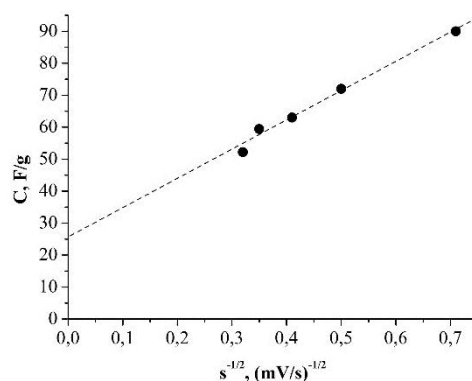


Fig. 7 – The dependence of C^{-1} on s for α -MnO₂

Since the value of C is linearly increasing with $s^{1/2}$, then $1/C$ should linearly decrease with $s^{1/2}$.

Therefore, $1/C = 1/C_{s=0} + b\sqrt{s}$ where $C_{s=0}$ is considerable gain in maximum specific capacity, b is a constant value (Fig. 7).

Table 1 – The capacity of a DEL and the maximum specific capacity

C_{DEL} , F/g	25.09
C_{max} , F/g	201.61
C_{DEL}/C_{max}	0.12

The reciprocal of the specific capacity linearly depends on $s^{1/2}$ Fig. 7.

It was possible to determine the maximum specific capacity of the material under investigation due to the extrapolation of the C^{-1} dependences on $s^{1/2}$ of the Y-axis (Fig. 7, Table 1). The charge/discharge characteristics of an electrochemical system based on α -MnO₂ electrodes are presented in Fig. 8. The discharge curves are characterized by two linear sections with different angles of inclination, which indicates two different mechanisms of electric energy storage.

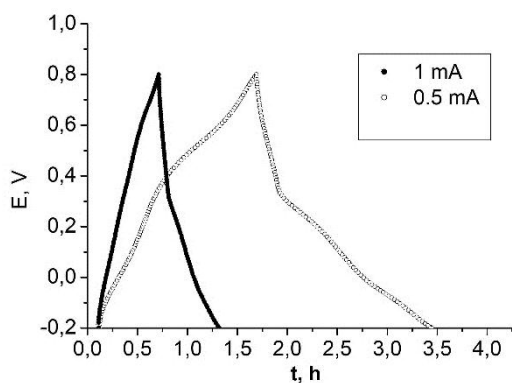


Fig. 8 – Charge/discharge curves

The specific capacity values of the MnO_2 /electrolyte materials at a discharge current of 0.5 mA considerate 0.92 mA h/g and at 1 mA – 0.71 mA h/g. The charge/discharge curve shows that a Coulomb efficiency of the electrochemical system is constant and independent of the cycle number under charge/discharge process.

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Синтез та електрохімічні властивості мезопористого $\alpha\text{-MnO}_2$ для застосування в суперконденсаторах

П.І. Колковський, Б.І. Рачій, М.І. Колковський, Б.К. Остафійчук, І.П. Яремій,
В.О. Коцюбинський, Р.В. Ільницький

ДВНЗ “Прикарпатський національний університет імені Василя Стефаника” вул. Шевченка, 57,
Івано-Франківськ 76018, Україна

В роботі досліджено електрохімічні властивості монофазного $\alpha\text{-MnO}_2$, отриманого гідротермальним методом. Встановлено, що отриманий матеріал володіє тунельною структурою із середнім розміром частинок 12-15 нм. Методами циклічної вольтамперометрії та гальваностатичного циклювання визначено питомі ємнісні характеристики синтезованого $\alpha\text{-MnO}_2$ у 30 % водному розчині КОН. Встановлено, що зі зростанням швидкості сканування з 2 до 10 мВ/с значення питомої ємності системи $\alpha\text{-MnO}_2$ /електроліт зменшується з 90 Ф/г до 55 Ф/г. Максимальне значення питомої ємності 104 Ф/г отримано при швидкості зміни потенціалу 0,5 мВ/с. Кулонівська ефективність електрохімічної системи є сталою і не залежить від кількості заряд/розрядних циклів. Загальну ємність електрохімічної системи розділено на ємність подвійного електричного шару і дифузійно-контрольовану окислювально-відновлювальну ємність за рахунок фарадеївських оборотних редокс реакцій, яка становить 90 % від загальної ємності. Крім того, встановлено, що електрохімічні параметри системи $\alpha\text{-MnO}_2$ /КОН є стабільними впродовж тривалого циклювання.

Ключові слова: Оксид марганцю, Псевдоємність, Гібридний електрохімічний конденсатор, КОН.

4. CONCLUSIONS

It was determined that the obtained $\alpha\text{-MnO}_2$ material is promising for use as the active component of HEC electrodes. The α form of MnO_2 with predetermined properties of channel structure, that is 0.46×0.46 nm, was obtained by hydrothermal synthesis. The capacity of manganese oxide is based on the effective use of the redox component, which allows to increase electrical conductivity of the $\alpha\text{-MnO}_2$ material by adding 10 % acetylene carbon black. The specific capacity value of $\alpha\text{-MnO}_2$ about 104 F/g at a scan rate of 1 mV/s was calculated based on data of the potentiodynamic method. A model of dividing the total capacity of the electrochemical system into the capacity of the C_{DEL} and the diffusion-controlled redox capacity due to the Faraday reverse redox C_F was proposed. Moreover, it was determined that capacity C_F is about 90 % of the total capacity of system. The stability of the structure and electrochemical parameters of the $\alpha\text{-MnO}_2$ sample under the cycle process was established.