

Effect of the concentration of MnO₂ in the composite electrode and the electrolyte on the electrochemical properties of a hybrid supercapacitor

G. D. Ivanova^{1*}, A. E. Stoyanova¹, M. A. Mladenov¹, R. G. Raicheff¹, D. G. Kovacheva²

¹*Institute of Electrochemistry and Energy Systems – Bulgarian Academy of Sciences, 10, G. Bonchev Str., 1113 Sofia, Bulgaria*

²*Institute of General and Inorganic Chemistry- Bulgarian Academy of Sciences, 11, G. Bonchev Str., 1113 Sofia, Bulgaria*

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A novel hybrid supercapacitor based on a composite of acetylene black and MnO₂ as positive electrode and activated carbon as negative electrode has been developed. The effect of the electrolyte (K₂SO₄, KOH and KOH+LiOH) and the concentration of MnO₂ in the composite electrode is investigated. A supercapacitor using 50 wt.% MnO₂/XC composite electrode and mixed KOH electrolyte demonstrates highest and most stable discharge capacitance (about 1400 cycles), as well as a highest effectiveness of the charge-discharge process. This result can be related one hand with the better electroconductivity of KOH solution in comparison to K₂SO₄ electrolyte and on the other - with the presence of Li⁺ ions, which favors the faradaic charge-transfer reaction.

Key words: hybrid supercapacitors, manganese dioxide, composite electrode material, alkaline electrolytes

INTRODUCTION

The supercapacitors (SCs) have emerged as one of the most attractive electrochemical energy storage systems featuring high power delivery and long-term cycling stability [1]. The application area of SCs is constantly growing as the new power sources arise from consumers in electronics to industrial and transportation [2].

Carbon-based active materials (AC) are the most widely used electrode materials in these systems due to their physical and chemical properties [3]. The integration of supercapacitors and batteries in energy storage and delivery systems gives a possibility to combine the high transient performance of the supercapacitors with high steady-state characteristics of the batteries. In order to improve the energy density while keeping long cycle life of the supercapacitors, hybrid electrochemical systems involving hybridization of a faradaically rechargeable battery-type electrode with an electrochemical double-layer capacitor-type electrode (e.g. asymmetric supercapacitors), are introduced. A prominent advantage of the hybrid cell is the enlarged operating potential window, which noticeably enhances the energy and power performance. In aqueous systems, this is of particular interest as it may allow the capacitor to be operated at a potential window wider than the water decomposition voltage of 1-2 V, if electrode materials with high overpotentials for hydrogen or oxygen evolutions are carefully selected [3,4]. One

particular issue with hybrid supercapacitors is non-linear charge-discharge, nevertheless promising results from various research groups indicated that this can be avoided by an appropriate cell fabrication [5].

Various hybrid capacitor configurations, consisting of activated carbon as a positive electrode and a negative electrode based on metal oxides (nickel, lead or manganese oxides) [6–8], conducting polymers [9] are suggested. The engineering of MnO_x with suitable materials of complementary properties to form a composite, or into specifically effective nanostructures to assist charge transport, represents an important direction of development. Appropriate cell configuration has been proven to be the necessity for the optimisation of the capacitive performance of MnO_x based supercapacitors. Based on these literature findings, the authors believe that manganese oxides represent a promising and very competitive electrode material for applications in supercapacitors [10] because of such superior characteristics as large specific capacitance, environmental benignity nature, natural abundance and low cost [11]. It was found that the textural characteristics, crystal forms and ion conductivity of MnO₂ strongly influence its electrochemical performances [12,13].

There are a lot of reports on MnO₂ preparation technologies, such as a co-preparation method, a thermal decomposition method, a sol-gel method

* To whom all correspondence should be sent.
E-mail: galia.ivanova2000@iees.bas.bg

and other methods [14-16]. Hybrid supercapacitors with MnO_x as the cathode and carbon materials such as activated carbon [17-20] as the anode have been fabricated. These hybrid systems exhibited superior capacitive behaviour in comparison with the symmetrical carbon based systems. A better cycling stability can be achieved, since the reduction of Mn⁴⁺ to soluble Mn²⁺ species, and hydrogen and/or oxygen evolution occurred when the hybrid cell was cycled over an operating potential window of 2.2 V [20].

However, MnO₂ suffers from low electronic conductivity and poor cation diffusivity, which results in poor utilization and limited rate performance of traditional MnO₂ powder electrodes, obtained by pressing a mixed paste of MnO₂ powder, conductive additive and polymer binder onto metallic current collectors [10].

The choice of electrolyte also has significant impacts on the performance of the MnO_x electrodes. The pH condition is an important determinant of the operating potential window; and different existing ions determine the rate of intercalation and the situation of corrosion. Thus, desirable electrode performance can be obtained only by choosing the composition of the electrolyte carefully [10].

It was reported that electrolyte with equal transference numbers for both cation and anion can promote capacitive behaviour and anions with smaller hydration sphere and smaller size leads to faster diffusion and higher chemisorption rates [21]. Experiments comparing the electrochemical performance of the MnO₂ material in several neutral aqueous electrolytes including NaCl, KCl and LiCl with the same concentration of 2 mol dm⁻³ have been conducted [21,22]. It was claimed that although Li⁺ is smaller than Na⁺ and K⁺, it has a larger hydration sphere, which makes it disadvantageous. And this theory was supported by the results from several other research groups [23,24]. However, a more recent study on the electrochemical behaviour of the MnO₂ electrode in 1 mol dm⁻³ KOH and 1 mol dm⁻³ LiOH [18, 25] declared that the reaction mechanism of MnO₂ electrode in LiOH appears to be Li⁺ ion insertion/extraction in the MnO₂ solid, followed by the battery reaction of MnO₂⁺ + Li⁺ + xe⁻ = Li_xMnO₂. This finding may elicit further thoughts upon the mechanism of the charge storage within MnO_x.

In our previous work it has been shown that Li⁺ ions and H₂O from the LiOH-KOH electrolyte are intercalated into α-Ni(OH)₂ and as a result, the α-Ni(OH)₂/AC displays an improved performance in the mixed LiOH-KOH electrolyte than that in the individual KOH electrolyte [26].

In this study we demonstrate the electrochemical properties of a novel type hybrid supercapacitor cell composed by two different electrodes – commercial MnO₂ (Fluka) (selected on the basis of our previous research [27]) with teflonized acetylene black (XC-35). The content of MnO₂ in the composite electrode is optimized in the range from 0 to 100%. Three types of aqueous electrolytes were used (0.1M K₂SO₄, 7M KOH and mixed electrolyte 7M KOH + 1.45 M LiOH) in order to study the effect of the electrolyte on the capacitive properties of MnO₂/XC-35 composite electrode. The structure and morphology changes of the composite electrode are monitored by X-ray Diffraction (XRD), Scanning and Transmission Electron Microscopy (TEM, SEM). The supercapacitor performance of the composite electrodes is tested by means of galvanostatic charge/discharge experiments.

EXPERIMENTAL

Physicochemical characterization of the electrode materials

The used materials are previously structurally characterized by X-ray Diffraction (XRD), Scanning and Transmission Electron Microscopy (TEM, SEM) [27, 28]. Powder X-ray diffraction patterns were collected within the range from 5.3 to 80° 2θ with a constant step 0.02° 2θ on Bruker D8 Advance diffractometer with Cu Kα radiation and LynxEye detector. The microstructure of the electrode materials is studied by means of JEOL JSM-5510 and JEOL Superprobe 733 scanning electron microscope (SEM) and JEOL 2100 Transmission electron microscope (TEM). The specific surface area is investigated by BET method using Area Meter, Strolen-Germany. The measurement is recorded by nitrogen gas adsorption at -197 °C. The samples are completely degassed by drying (100°C), thermostating (120°C), and blowing with nitrogen.

Preparation of supercapacitor cells and electrochemical testing

The hybrid supercapacitor cell is composed by a positive electrode – a composite of teflonized acetylene black (XC-35) and commercial MnO₂ in concentration range from 0 to 100 wt.%, and a negative electrode of activated carbon (Cabot CGP Super) with addition of PTFE and carbon black (Cabot SC2). The formed sheet electrodes (surface area 1.75 cm²) were dried at 140°C for 12 hours and pressed under pressure of 20 Mpa, soaked in the electrolyte under vacuum and then mounted in a coin-type cell with Viledon 700/18F separator and filled with electrolyte. Three types of alkaline

solutions were used as electrolytes: 0, 1 M K_2SO_4 solution, 7 M KOH solution and 7 M KOH solutions with additives of 35 $g\ l^{-1}$ LiOH (i.e. 1,45M LiOH). The capacitor cells were subjected to galvanostatic charge-discharge cycling using an Arbin Instrument System BU-2000. The test program was carried out at constant current mode at different current load (from 30 to 360 $mA\ g^{-1}$) and room temperature [28]. Some cells are subjected to continuous cycling charge/discharge at current rate of 60 $mA\ g^{-1}$ up to 1400 cycles.

RESULTS AND DISCUSSIONS

Physicochemical characterization

The powder diffraction pattern of the active materials used (Cabot CGP Super and MnO_2) are presented in Fig. 1. It is seen that Cabot CGP Super and MnO_2 differ in their phase composition and size of the crystallites.

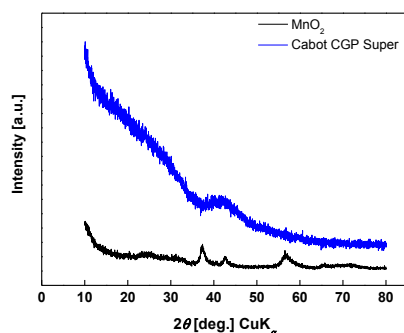


Fig.1. XRD pattern of the Cabot CGP Super and MnO_2 [26, 27]

On the powder pattern of the activated carbon typical amorphous humps are observed in the range 20-25 degrees, which corresponds to (001) reflections of the graphite and 38-48 degrees corresponding to (101) diffraction of the graphite. The pattern of MnO_2 -sample shows a single phase MnO_2 – akhtenskite type structure with crystallites sizes about 5–6 nm.

The TEM images of the activated carbon and manganese dioxide illustrate their structural and morphological characteristics (Fig. 2).

The high specific surface area and high distribution of the Cabot CGP Super material and all textural parameters suggest that it is an appropriate electrode material for carbon electrodes in supercapacitor systems (Fig. 2a), consisting mainly of small particles clusters. The micrographs of MnO_2 (Fig. 2b) demonstrate crystalline structures with homogeneous definition of crystalline grains and nanosized particles.

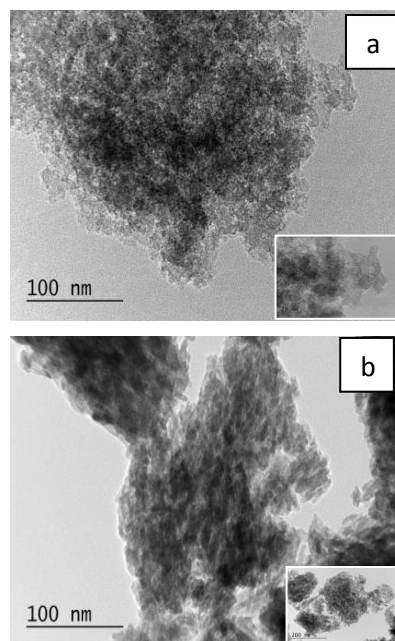


Fig. 2. TEM images of Cabot CGP Super(a) and MnO_2 (b)

The pore textures of the activated carbons are studied by taking the nitrogen adsorption/desorption isotherms of the samples. The results show that the Cabot CGP Super possesses a very high surface area (1825 $m^2\ g^{-1}$) and large micropore volume independently from the smaller total pore volume [28]. The specific surface area on MnO_2 is 58.80 $m^2\ g^{-1}$.

Electrochemical performance of the supercapacitor cells

The electrochemical performance of the supercapacitor cells developed are studied by charge/ discharge cycling test under identical experimental conditions, at different (increasing in values) constant current loads with minimum 25 cycles at each current rate.

Figure 3 gives the dependences of the specific discharge capacity on the current load for the supercapacitor cells free of manganese dioxide with different electrolytes (0,1M K_2SO_4 , 7M KOH with and without addition of LiOH). The analysis of the cycling behaviors shows that the asymmetric supercapacitor cells using mixed electrolyte (KOH+LiOH) demonstrate highest discharge capacity compared to the other two cells (about 15-17% higher than the cell without LiOH and about 50% than the supercapacitors with K_2SO_4).

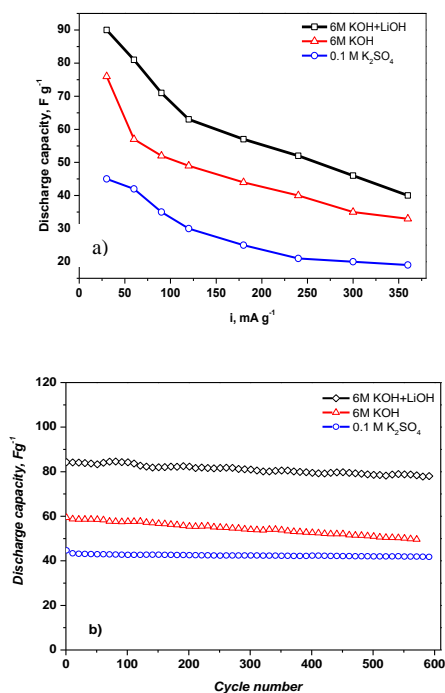


Fig. 3. Dependence of the discharge capacity on the current load (a) and on the cycle number at current load 60 mA g^{-1} (b) for the supercapacitor cells free of manganese dioxide

The relation in figure 3a shows that the discharge capacity for the supercapacitor free of manganese dioxide with mixed electrolyte is very stable at prolong cycling and after 600 cycles it drops only by about 7 - 10%. The discharge capacity for the supercapacitors cell using 0,1M K_2SO_4 is very stable too, but its values are the lowest, while in pure KOH it is less stable and with lower values than in the presence of a small amount of LiOH. Obviously Li^+ ions from the electrolyte display a positive effect on the discharge capacitance and the cycling stability of the supercapacitor performance.

Figure 4a gives the dependences of the discharge capacitance as a function of discharge current density and cycle number for supercapacitors with composite electrodes containing 0 – 100 wt.% MnO_2 while the dependence of the discharge capacitance on the MnO_2 content, determined at low and high current loads, is illustrated on Figure 4b. Irrespective of the current loads, the discharge capacitance curve passes through a maximum between 40 and 60% wt.% MnO_2 , as the highest capacitance value being observed at 50 wt.% MnO_2 .

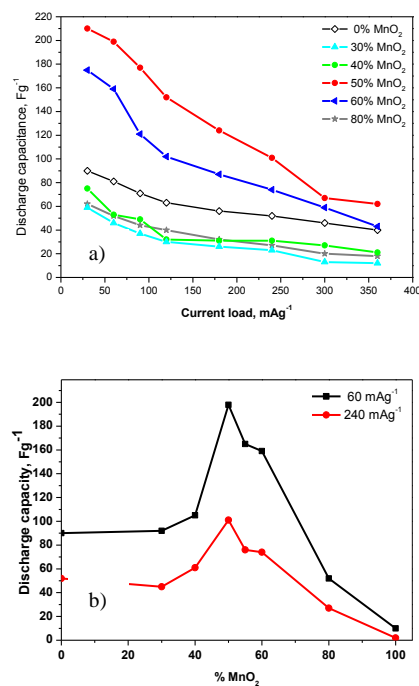


Fig. 4. Discharge capacitance for supercapacitors with MnO_2 in various content as a function on the current load (a) and on the MnO_2 content at different current loads (b)

The hybrid supercapacitors demonstrate a higher and a stable discharge capacitance, as well as a higher effectiveness of charge-discharge process, in the whole range of current loads. Above 80 wt.% and below 30 wt.% of MnO_2 the discharge capacitance of the hybrid capacitors becomes lower than that of the supercapacitor free of manganese dioxide. This non-monotonous dependence can be related with formation of composite electrodes, where double layer capacitance and Faradaic pseudocapacitance are expected to be active. Below 30 wt.% of MnO_2 , it appears that homogeneous composites XC/ MnO_2 with improved electrical conductivity are formed due to the high porosity of XC (58,13% [29]). Above 35 wt.% of MnO_2 , the reduction of AC content leads to a decrease of the electrical conductivity of the electrode, as a result of which the discharge capacitance decreases [30].

The effect of the alkaline electrolyte on the hybrid supercapacitor performance is investigated using XC/ MnO_2 as composite electrode. Figure 5 shows the dependence of the discharge capacity of the hybrid supercapacitors a function on the current load in different alkaline electrolytes. The dependence here is the same as for the supercapacitor free of manganese dioxide (Fig. 3a) and the discharge capacitance values are higher. The increasing here is about 40% at 60 mA g^{-1} and at higher current load (240 mA g^{-1}) the effect of Li^+

decreases (24%), but the discharge capacitance in K_2SO_4 solution increases significantly to about $20Fg^{-1}$ (the value of the discharge capacitance in KOH+LiOH electrolyte here is $100Fg^{-1}$).

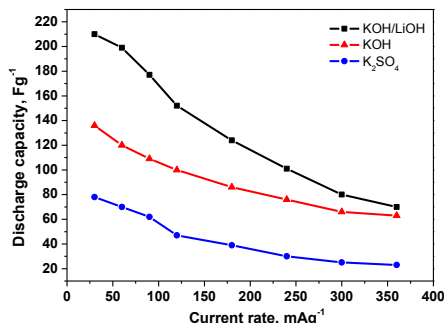


Fig. 5. Dependence of the discharge capacity of hybrid supercapacitor on the current load at different electrolytes

Figure 6 shows charge/discharge curves of the 50 wt.% MnO_2/XC composite electrode working in different electrolytes. All three devices exhibit galvanostatic charge–discharge curves which resemble those of electrochemical double layer capacitor. However, a closer look indicates that the slopes of the three systems slightly differ from linearity as a result of the pseudo-Faradaic processes for the oxide electrodes [8]. This trend is more pronounced for the device using K_2SO_4 as electrolyte. This supercapacitor has the lowest capacitance, despite its enhanced cell potential compared to cells using KOH as an electrolyte. The reason for the lower capacity in sulfate solution is probably due to its lower conductivity compared to that of 7M KOH.

As can also be seen from Fig. 6, the iR -drop of the supercapacitor in the mixed LiOH-KOH electrolyte is slightly lower than that in the two others electrolytes: 0.20 V (LiOH-KOH) versus 0.24 V (KOH) and 0.29 V (K_2SO_4) respectively. This results in a high discharge capacitance of the supercapacitor working with mixed LiOH-KOH electrolyte.

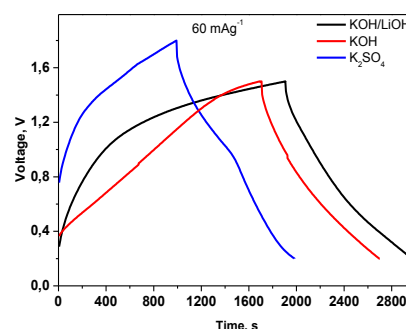


Fig. 6. Galvanostatic charge and discharge curves of hybrid supercapacitor with 50 wt.% MnO_2 in the composite electrode

The improved capacitance can be related with a change in the conductivity of the mixed LiOH-KOH electrolyte. Furthermore, the higher discharge capacitance in the mixed LiOH-KOH electrolyte can be related also with the reaction mechanism for energy storage. The appearance of Li^+ ions in the alkaline electrolyte favors, in addition to the capacitive reactions, the reactions that take place by a faradaic charge-transfer mechanism [28]. The redox reaction in the MnO_2 electrode can be viewed as the reversible insertion/extraction of Li^+ in MnO_2 solid, which is different from the case of using pure KOH electrolyte, and this can explain the significantly higher capacity increase in hybrid supercapacitors in mixed electrolyte [25].

As it is seen, the hybrid supercapacitor based on anode material with 50% manganese oxide in the composite electrode exhibits the highest discharge capacity in mixed solutions and because of this in Fig. 7 are shown its electrochemical characteristics. The proposed supercapacitor exhibits high discharge capacitance (above $200Fg^{-1}$) and high efficiency (97- 98%) and stable cycle life (above 1400 cycle).

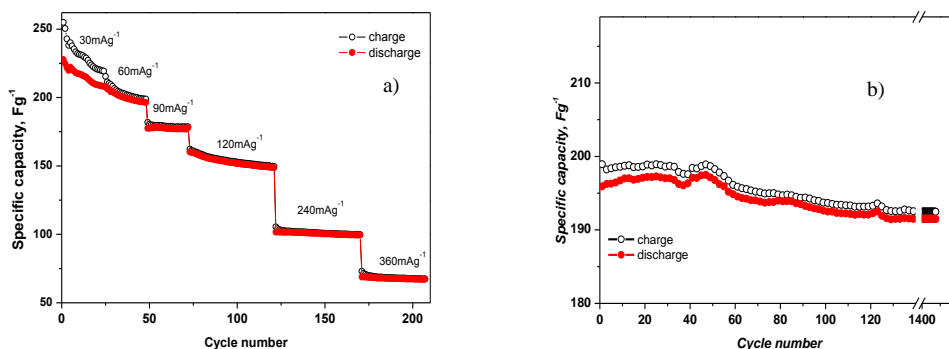


Fig. 7. Discharge capacitance as a function of the current load (a) and the cycle number at current load 60 mA g⁻¹ (b) of hybrid supercapacitors with composite electrode containing 50 wt% MnO₂/XC and mixed electrolyte of 7 M KOH with addition of LiOH

CONCLUSIONS

A novel hybrid supercapacitor based on a composites of acetylene black (XC-35) and commercial MnO₂ as positive electrode and activated carbon as negative electrode using three different electrolytes (0,1M K₂SO₄, 7M KOH and mixed electrolyte 7M KOH + 1.45 M LiOH) has been developed. The ratio between MnO₂ and acetylene black is varied in a whole concentration range from 0 to 1,0. The supercapacitors with 50 wt. % MnO₂ and mixed electrolyte KOH + LiOH demonstrate highest and most stable discharge capacitance, as well as a highest effectiveness of charge-discharge process. The better performance of the composite electrode in the mixed electrolyte is related with the better electroconductivity of KOH solution in comparison of K₂SO₄ and the presence of Li⁺ ions, which favors the faradaic charge-transfer reaction.

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ВЛИЯНИЕ НА КОНЦЕНТРАЦИЯТА НА MnO_2 В КОМПОЗИТНИЯ ЕЛЕКТРОД И НА ЕЛЕКТРОЛИТА ВЪРХУ ЕЛЕКТРОХИМИЧНИТЕ СВОЙСТВА НА ХИБРИДНИ СУПЕРКОНДЕНЗАТОРИ

Г. Д. Иванова^{1*}, А. Е. Стоянова¹, М. А. Младенов¹, Р. Г. Райчев¹, Д. Г. Ковачева

¹Институт по електрохимия и енергийни системи – Българска академия на науките, ул. Акад. Г. Бончев 10, 1113 София

²Институт по обща и неорганична химия – Българска академия на науките, ул. Акад. Г. Бончев 11, 1113 София

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(Резюме)

Разработен е нов хибриден суперкондензатор на базата на ацетиленови сажди и MnO_2 като положителен електрод и активен въглен, като отрицателен електрод. Изследван е ефектът на електролита (K_2SO_4 , КОН и КОН+LiОН) и концентрацията на MnO_2 в композитния електрод. Суперкондензаторите с композитен електрод, съдържащ 50 тегл.% MnO_2 и смесен електролит на КОН+LiОН показват най-висок и най-стабилен разряден капацитет (до 1400 цикъла), както и най-висока ефективност при зарядно-разрядния процес. Този резултат се дължи от една страна на по-добрата електропроводимост на КОН в сравнение с K_2SO_4 , а от друга страна - на наличието на Li^+ йони, които благоприятстват Фарадеевата реакция.

Ключови думи: хибридни суперкондензатори, манганов диоксид, композитен електроден материал, алкален електролит