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Activated nano-porous carbons as electrode materials for supercapacitors in aqueous electrolyte

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In the present work is studied the effect of two types binders (polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE)) on the pore structure of chosen nanocarbons as electrode materials for symmetric supercapacitors. The PVDF influences both the micro and macro pores, while PTFE attacks preferentially the macropores. The commercial product TDA-Research with PTFE binder, which possess the highest micropore volume and micropore surface, shows the highest and stable discharge capacity in comparison to both other studied carbons.
The addition of 6.2% β-$Ni(OH)_2$ to the positive electrode in the supercapacitor increases the discharge capacity significantly (around 35-40% at 30-60 mAg^{-1}). The obtained result is promising and it deserves further examination.

Keywords: activated nanocarbon, binder, supercapacitor, aqueous electrolyte, $Ni(OH)_2$

INTRODUCTION

In the recent years many research groups work on the development and the use of alternative energy sources in order to respond to the enhanced needs of light and compact high capacity sources [1].

Among the various realistic solutions, energy can in particular be stored electrochemically in accumulators (batteries) and supercapacitors. Supercapacitor is one of the most promising electric energy storage devices, which possesses high power density, ultrafast charge discharge capability as well as long cycling life. It has a great application potential in the fields of hybrid electric vehicles (HEVs), EVs, portable electronic devices, and renewable energy [2].

Recently, supercapacitors have been proposed and widely marketed for variousapplications. Coupled for example with a battery/internal combustion engine in hybrid vehicles, supercapacitors improve the battery lifetime/fuel economy and the energy recovery efficiency in braking. They can also stabilize current when intermittent renewable energies are introduced in the energetic mix [3].

Although supercapacitors are now commercially available, they still require improvements, especially for enhancing their energy density and cut the cost at the same time. It requires a fundamental understanding of their properties and exact operating principles, inaddition to improving electrode materials, electrolytes and integration in systems.

The physical and electrochemical characteristics of used materials are very important for the development of supercapacitors. A very important problem is associated with the physical gas phase properties of nanoporous material, like the nanopore diameter and pore size distribution, the conductivity and the accumulation of energy in the space-charge surface layer, i.e., the so-called capacitance of the thin layer obtaining the characteristic relaxation frequencies, specific energy and power densities and other characteristics of the supercapacitors [4].

A various carbon materials are investigated as electrode materials for electrical double-layer capacitors, owing to their high conductivity and surface area, a rich variety of dimensionality, excellence corrosion resistance, high thermal stability, controlled pore size distribution, processability andcompatibility in composites, relatively low cost, etc. It is usually anticipated that the capacitance of the porous carbon should be proportional to its available surface-area. In practice, the major factors that contribute to this relationship, often with a complex non-linear character, are: the assumptions in the measurement of electrode surface-area, variations in the specific capacitance with differing morphology and pore-size distribution, variation in surface chemistry, conductivity of the carbon particles, etc. There are contradictory reports in the literature on the effect of increasing surface area and porosity on the intrinsic electronic conductivity of compact carbon

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powders, but the presence of micro pores is very desirable. A developed surface area and controlled distribution of pores for porous carbons, produced by well established chemical and physical activation methods, determine the electrode/electrolyte interface in supercapacitor applications [5-7].

Activated carbon is the most widely used active material due to its high surface area and relatively low cost. Its activation is used for the addition formation of porous network in the bulk of the carbon particles with high specific surface area [8]. Other advantage of those materials is the possibility to produce highly porous structures with high specific surface area and to develop various composite electrode structures by adding electrochemically active materials to the carbon matrix [4].

Further improvement of the performance of activated carbon can be achieved by a modification with transition metal oxides or hydroxides. Recently, β-Ni(OH)$_2$ has been proposed as a suitable agent for the modification of electrochemical properties of carbonaceous materials [9-12]. It has been shown that the capacity of hydroxide modified carbonaceous materials increases at the expense of the loss of cyclic stability. In fact, an ideal performance of supercapacitors included high capacitance, good stability and wide voltage window, its mass balance needs reevaluation [13]

By the construction of the supercapacitor electrode the metallic current collector is coated by slurry containing the electrochemically active material (activated carbon) together with a binder and the conductive agents (carbon black, etc.) playing as percolator between the AC grains [9]. The nature of the binder plays an important role for the capacitor performances too. The most used materials are polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE).

The electrolyte also plays an important role in the supercapacitors performance. The electrolyte must possess certain properties, such as high ionic conductivity, wide voltage window, and high electrochemical and thermal stability, low viscosity, low toxicity, low cost, etc. The currently used electrolytes are aqueous electrolytes (H_2SO_4 and KOH), organic electrolytes (propylene carbonate and acetonitrile based ones), and recently ionic liquids [14]. Compared with non-aqueous electrolytes, the aqueous medium provides a much higher conductivity leading to higher power density. On the other hand, low cost and easy manipulation could be further advantages for aqueous electrolytes. Unfortunately, the lower voltage of aqueous medium is restricted via the thermodynamic window of water at 1.23 V and it is much lower than in non-aqueous electrolytes [15].

The aim of the present work is to study effect of the binder on the pore structure of chosen carbons (commercial and synthesized products) as electrode materials for symmetric supercapacitors in alkaline solutions on their capacitance behavior. The modification of the positive electrode with 6.2% β-Ni(OH)$_2$ is also electrochemically tested.

EXPERIMENTAL

Electrode materials

In the present work three kinds of activated carbons are studied as electrode materials for supercapacitor cells – two commercial products (TDA-Research and Norit-CGP) and one synthesized carbon (AC-1400). AC-1400 is prepared by carbonization of mixtures of coal tar pitch and furfural, with a subsequent hydrothermal treatment [4]. As an additive commercial β-Ni(OH)$_2$ containing 4.2% Co (FC05(III), Umicore Cobalt & Specialty Materials) is used.

Morphological and structural characterization of the electrode materials

The materials used are structurally characterized by X-diffraction (XRD) method. The powder X-ray diffraction patterns are collected in the range from 5.3° to 80° 2θ with a constant step of 0.02° 2θ angle on Bruker D8 Advance diffractometer with Cu Kα radiation and Lynx Eye detector. Phase identification was performed with the Diffractplus EVA using ICDD-PDF2 Database.

The morphology of the electrode materials is examined by Transmission electron microscopy (TEM).

The pore structure of the carbons is evaluated by nitrogen gas adsorption. The adsorption isotherm of the sample at −196 °C is recorded and used to calculate the specific surface area, pore volumes and pore size distributions [4].

Electrochemical tests

The activated carbon materials are used to fabricate electrodes for electrochemical cells for capacity measurements. The supercapacitor cell contains two identical electrodes (surface area ~1.75 cm^2) from activated carbon (80%), graphite ABG 1005 EG-1 (10%), binder (10%) and alkaline electrolyte containing potassium hydroxide with the addition 35gL^{-1} lithium hydroxide (7M KOH/LiOH) [15]. The electrodes are fabricated by applying two kinds of binders: PTFE (Polytetraflourethylene) and PVDF (polyvinylidene difluoride). The supercapacitor cells are assembled with the addition of 6.2% β-Ni(OH)$_2$ to the positive electrode.

The formed sheet electrodes are dried at 140 °C for 12 hours and pressed under pressure of 20 MPa. The obtained electrodes are soaked in the same electrolyte under vacuum and then mounted in a coin-type cell with Glassmat separator and filled with electrolyte. The capacitor cells were subjected to galvanostatic charge-discharge cycling using an Arbin Instrument System BU-2000 [16, 17]. The test program is carried out at constant current mode at different current load (from 30 to 360 mAg^{-1}) at 25 cycles and room temperature. Some cells are subjected to continuous cycling charge/discharge at current rate 60 mAg^{-1} up to 700 cycles.

RESULTS AND DISCUSSIONS

Physicochemical characteristics

Figure 1 shows powder X-ray diffraction patterns of the carbonaceous materials. Both commercial TDA-Research and Norit-CGP samples display typical amorphous hums in the range of 20-25º and of 38-48º, respectively. These not-well resolved diffraction peaks are due to (00l) and (101) diffraction planes of the graphite–type structure. The XRD pattern of Norit-CGP sample shows lower value of graphitization in comparison to the TDA-Research sample [18]. The XRD pattern of AC-1400 shows several stronger amorphous “humps”, located at 2θ values of about 24.5º and 43.5º, corresponding to the (002) and (100)+(101) peaks of 2H-hexagonal crystalline graphite and indicate the formation of graphite domains with higher crystallite sizes [19].

Table 1 summarized the data on specific surface area and pore volume for carbonaceous materials. For each of the materials, there are three types of pores - micro, mezo and macro, conventionally divided according to their size. Although the TDA-Research sample exhibit mainly micro pores (about 80% of the total pore volume), the other two samples AC-1400 and Norit-CGP are characterized with 70% and 30% of micropores, respectively. It is seen that the investigated carbons have very high specific surface area, as the micropore volume of TDA-Research is the highest compared to the two other carbon materials.

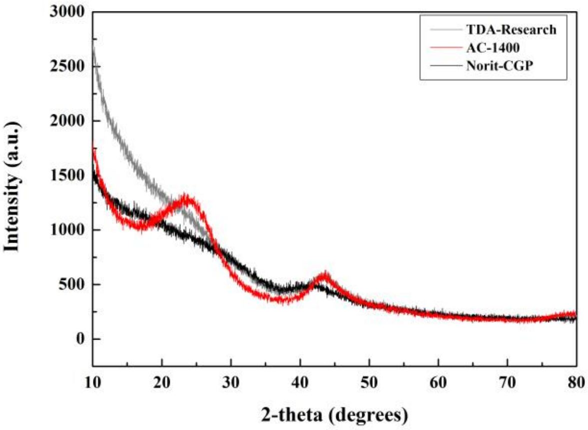

Fig. 1. XRD patterns of the used carbon material.

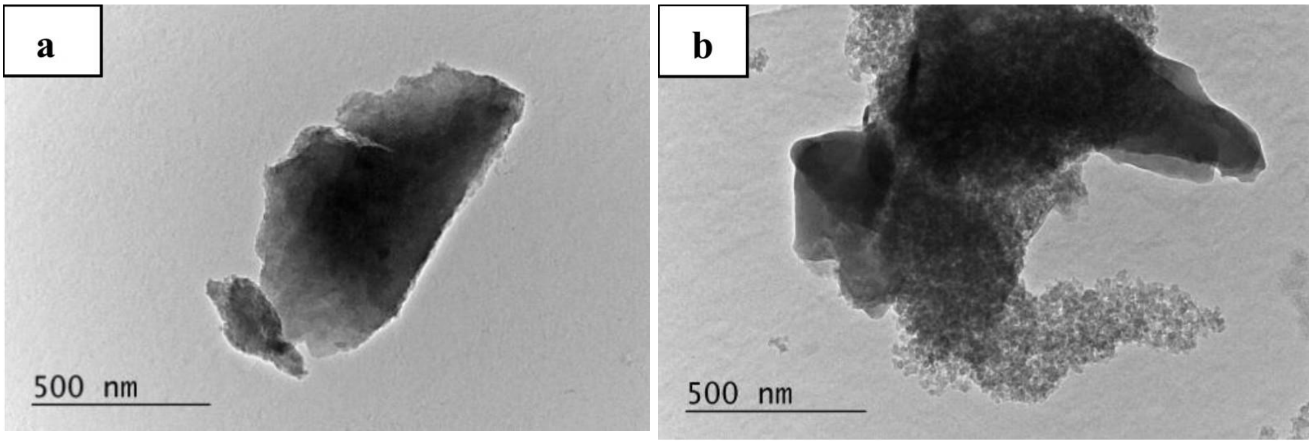

Fig. 2. TEM image of activated carbon samples: TDA Research (a) and Norit-CGP (b).

The TEM images show that for TDA-Research sample the large plate-like aggregates dominate, while the Norit-CGP carbon consists of both plate-like aggregates and small thin particles (Fig. 2). In AC-1400, there are mainly small particles. All these data suggest that Norit-CGP surface is highly developed, which corresponds to the data from Table 1.

Electrochemical characteristics

The assembled symmetric capacitance cells with different activated carbons and binders are electrochemical studied at constant current charge–discharge mode in the voltage window 0.1-1.0 V and at low current density of 60 mAg^{-1} during prolonged cycling (700 cycles). The specific discharge capacitance of the electrodes was calculated according to [20].

The value of the specific capacity C is obtained from the charge-discharge cycling measurements according to the following equation:

$$C = 4\ I\ \Delta t\ /\ m\ \Delta V \qquad (1)$$

where I, Δt, ΔV and m are respectively, the constant current applied, charge/discharge time, voltage window and the total mass of the electrode material.

Figure 3 gives the dependences of the discharge capacity as a function of discharge current density for studied carbon electrodes fabricated by using PVDF and PTFE as binders. The comparison shows that the structure of the binder plays a significant role on the supercapacitor performances. By using of PVDF as a binder (Fig. 3a), it appears that the electrochemical performances of three types of carbonaceous materials are similar. Contrary, the discharge capacity curves of supercapacitators with different carbons and PTFE as a binder are essential different. The highest capacity values are observed for commercial AC-TDA Research in the whole range of current rates. In the system with AC Norit-**CGP the** capacity drastically reduced (Fig. 3b).

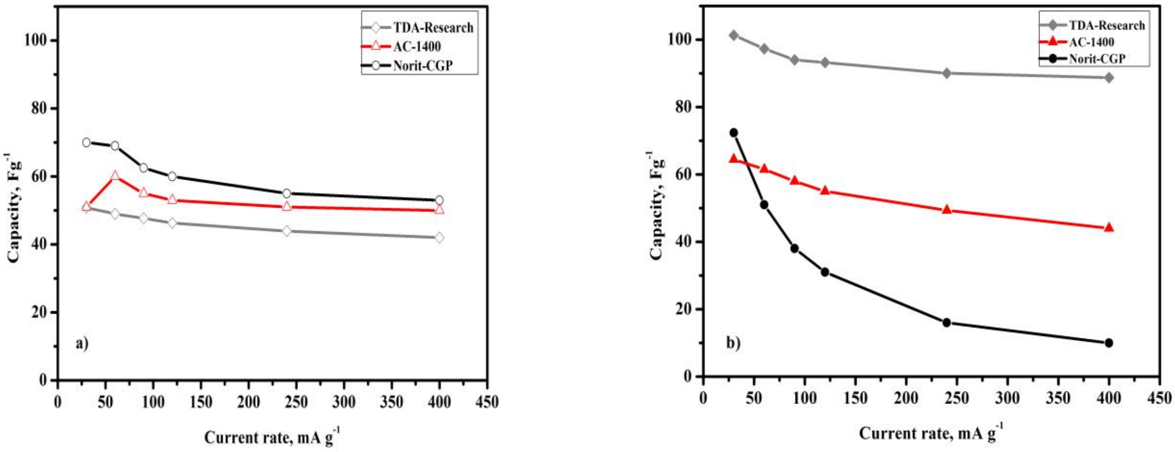

Fig. 3. Dependence of the discharge capacity of supercapacitors with different carbons on the current load: a) PVDF-binder and b) PTFE-binder.

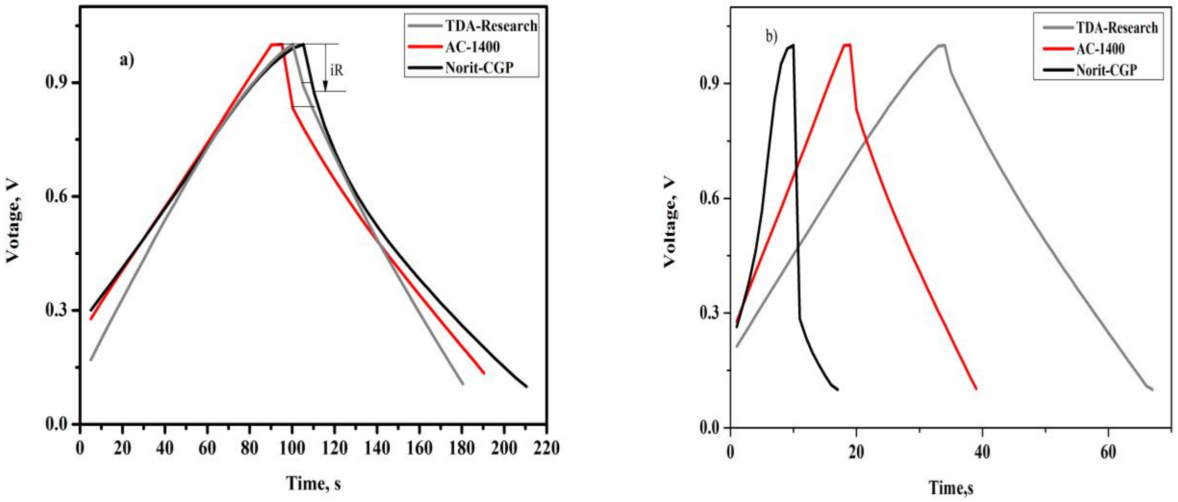

Fig. 4. Galvanostatic charge-discharge profiles of activated carbons with different binders: a) PVDF and b) PTFE at current rate 240 mAg^{-1}

To rationalize the effect of the binder on the electrochemical performance of carbonaceous materials, Figure 4 illustrates the charge-discharge profile curves of all studied samples fabricated in electrodes with PVDF and PTFE-binders. The profiles of all curves shown are typical for supercapacitor systems, and here it is evident the influence of the binder on the capacitive properties of nanoporous carbons as electrode materials. From the discharge curves, the "ohmic potential drop" (iR-drop) can be calculated, the values being giving in Table 1. The iR drop has a great influence on electrochemical measurements, and their effects should be considered during the interpretation of electrochemical data.

Table 1. Pore parameters of the carbon materials: activated surface (S_{BET}), total pore volume (V_{tot}), micropore volume (V_{micro}) micropore surface (S_{micro}) of activated carbon samples and iR-drop.

Sample	S_{BET}, m^2g^{-1}	V_{tot}, cm^3g^{-1}	V_{micro}, cm^3g^{-1}	S_{micro}, m^2g^{-1}	iR^{PTFE}, V (at 240 mAg^{-1})	iR^{PVDF}, V (at 240 mAg^{-1})
AC-1400	1400	0.630	0.453	1008	0.17	0.17
TDA- Research	1524	0.680	0.550	1234	0.08	0.11
Norit-CGP	1825	1.400	0.380	495	0.71	0.12

As one can see, the calculated values of IR-drop are close for carbonaceous materials fabricated in electrodes with a PVDF binder, while for the PTFE-binder there is a clear tendency for increasing the IR-drop for AC-1400 having lowest micropore volume. These results suggest that the PVDF binder affects both micro and macro pores, as a result of which the capacitive values are close for all samples studied irrespective of their porous structure. In addition, Norit-CGP has a largest surface and the highest discharge capacity is observed in this case.

The presence of PTFE in the electrode, however, substantially alters the electrochemical characteristics of the supercapacitors, since it preferentially influences the macropores. The highest capacity values, excellent cycle ability and very stable capacity at prolong cycling are registered for commercial AC-TDA Research with PTFE-binder compared to other tested materials. This carbon possesses much high micropore surface area and the highest micropore volume (Tabl.1) and significantly lower resistance compared to Norit-CGP (around 9 times at 240 mAg^{-1}).

Figure 5 compares the charge-discharge profiles at low and high current loads (60 and 240 mA g^{-1}) of supercapacitors with TDA-Research based electrodes assembled with the both PVDF and PTFE binders. The curve profiles and the calculated iR-drops show that already at low current density, the electrode resistance with PVDF-binder is higher than that with PTFE. This is in agreement with the suggestion that the electrode binder acts differently on the macro- and micro pores of the nanocarbons and thus on their adsorption ability.

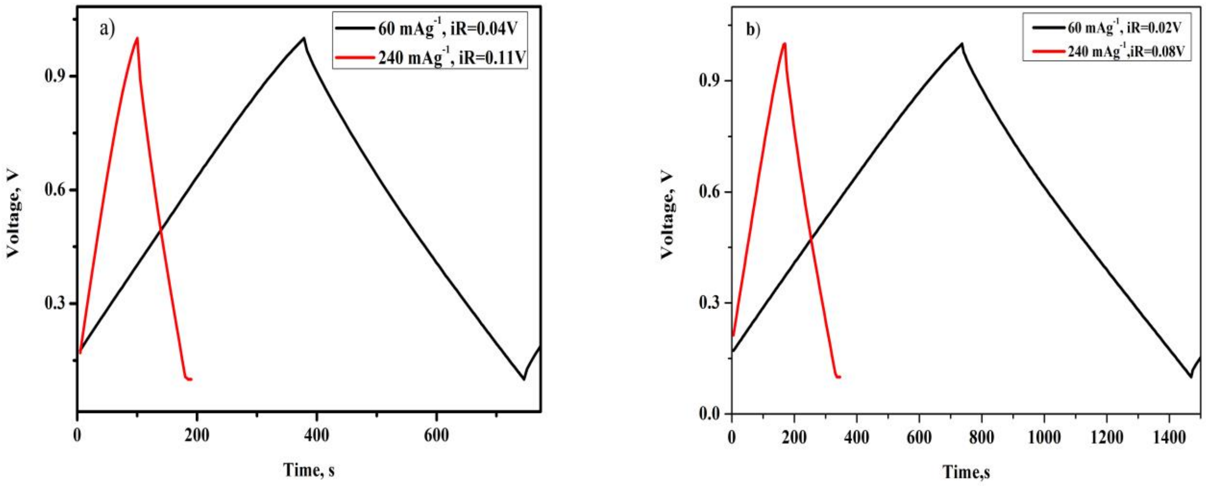

Fig. 5 Galvanostatic charge-discharge profiles of TDA Research with different binders: a) PVDF and b) PTFE at current rates 60 and 240 mAg^{-1}.

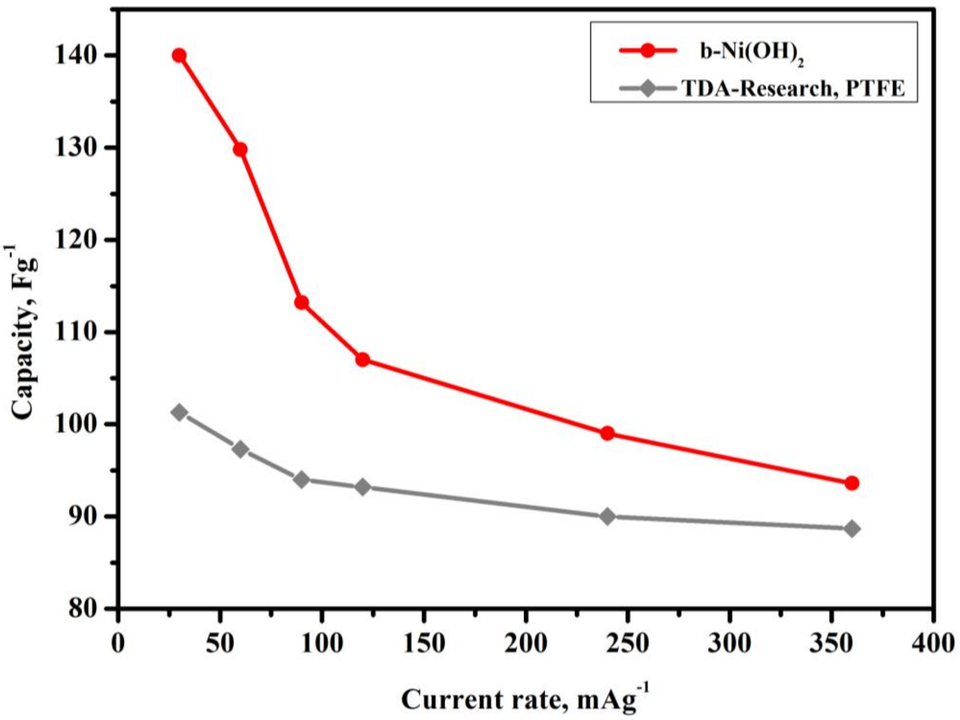

Fig. 6. Dependence of the discharge capacity of supercapacitors with TDA-Research /PTFE and modified with 6.2% $Ni(OH)_2$ on the current load.

Based on the best electrochemical performance of TDA-Research sample with PTFE binder, we further modified the properties of the sample by β-$Ni(OH)_2$ (Fig. 6). The electrochemical cell consists of TDA-Research/PTFE as a negative electrode and modified with 6.2% β-$Ni(OH)_2$ TDA-Research/PTFE as a positive electrode.

The comparison of the capacity-discharge current plots shows that the addition of small amount of β-$Ni(OH)_2$ to the positive electrode in the supercapacitor increases the discharge capacity significantly (around 35-40% at 30-60 mAg^{-1}) at low current density. This effect of β-$Ni(OH)_2$ becomes smaller when higher current density is used. This result implies that at low current density, the mechanism of the electrochemical reaction is changed. The obtained result is very interesting and it deserves further examination.

CONCLUSIONS

Three types of activated nanoporous carbons having different micropore structure are investigated as electrode materials for supercapacitors. It was found that the binder affect strongly their electrochemical characteristics, acting differently on the pore structure. The PVDF binder influences both the micro and macro pores, while PTFE attacks preferentially the macropores. The highest and stable discharge capacity demonstrates the commercial activated carbon TDA-Research (USA) with PTFE binder, which possesses the highest micropore volume and surface.

The modification of the positive electrode with 6.2% β-$Ni(OH)_2$ increase the discharge capacity by around 35-40 Fg^{-1} at low current density.

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АКТИВИРАНИ НАНОВЪГЛЕРОДИ КАТО ЕЛЕКТРОДНИ МАТЕРИАЛИ ЗА СУПЕРКОНДЕНЗАТОРИ ВЪВ ВОДЕН ЕЛЕКТРОЛИТ

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(Резюме)

В настоящата работа е изследван ефектът на два вида свързващи вещества (polyvinylidene fluoride (PVDF) и polytetrafluoroethylene (PTFE)) върху структурата на порите на избрани наноразмерни въглероди като електродни материали за симетрични суперкондензатори. PVDF оказва влияние върху микро- и макропорите, докато PTFE атакува приемуществено макропорите. Търговският продукт TDA-Research със свързващо вещество PTFE, притежаващ най-висок обем и повърхност на микропорите, показва най-висок и стабилен разряден капацитет спрямо останалите два вида изследвани въглероди.

Добавката на 6.2% β-$Ni(OH)_2$ към положителния електрод на суперкондензатора увеличава съществено разрядния му капацитет (с около 35-40% при 30-60 mAg^{-1}). Полученият резултат е многообещаващ и изисква по-нататъшни изследвания.