



High powered hybrid supercapacitor with microporous activated carbon

K. Shree Kesavan, K. Surya, M.S. Michael*

Department of Chemistry, SSN College of Engineering, Chennai 603110, Tamilnadu, India



ARTICLE INFO

Keywords:

Activated carbon
Microporous
Symmetric capacitor
Hybrid capacitor
MnCo₂O₄

ABSTRACT

Uniformly sized micropores of < 1 nm size are generated in petcoke by activating it with an alkaline solution, KOH. The influence of nano-confinement effect of these micro pores on electrochemical performance of the Activated Carbon (mAC) is investigated in symmetric as well as hybrid capacitor configuration, employing different aqueous namely acidic (0.5 M H₂SO₄), alkaline (2 M KOH), neutral (1 M KCl) and non-aqueous electrolytes (1 M TEA-BF₄ in 1:1 DC & EC). Despite of high ionic conductivity of these aqueous electrolytes, symmetric capacitors exhibit poor rate capability because of the restricted entry of solvent sheath into the micropores which strengthens the ionic interaction and slow down the diffusion of ions at high current rate. On the other hand, the overflowing electrolyte from the micropores of mAC appears to enhance the rate of diffusion of ions into nanostructured pseudocapacitive binary metal oxide, MnCo₂O₄ in the hybrid configuration and improves its power rate capability significantly. The superior capacitive performance of hybrid capacitor demonstrates that the possibility of solving the inherent limitation of micro porous electrodes by coupling it with nanostructured pseudocapacitive material. In the present work, high specific power, 6805 W kg⁻¹ and high specific energy, 2.64 Wh kg⁻¹ have been achieved with the hybrid capacitor of configuration mAC||KOH||MnCo₂O₄ at a high current rate, 30 A g⁻¹.

1. Introduction

Supercapacitors (SCs) also called Electric Double Layer Capacitors (EDLC), Ultracapacitors, Electrochemical capacitors (ECs) are gaining more attention in recent years due to their high energy and power density. SCs can be used in portable electronic devices, back-up power storage and hybrid transportation systems, because of their attractive characteristics of a short time for the recharge (~10⁴) [1–4]. Based on the mechanism of storage, SCs are classified into two categories, namely electric double layer capacitors (EDLCs) and pseudocapacitors [5]. EDLCs store energy by an accumulation of charges at the interface of electrode and electrolyte without any charge transfer [6–8], while the energy storage in pseudocapacitors is ruled by quick redox processes involve charge transfer across the electrode/electrolyte interfaces. Pseudocapacitance is generally observed in transition metal oxides and conducting polymers [9–12]. The specific energy of pseudocapacitors is higher than that of EDLCs because of faradaic reaction but their power rate capability is much lower than that of latter because of poor electronic and ionic conductivity of transition metal oxides and poor stability of conducting polymer.

The performance of supercapacitor is governed by the specific capacitance of electrodes, potential window, the electronic/ionic conductivity of the electrodes, porosity of electrode materials and

conductivity of the electrolyte. Generally, electrolytes with the high potential stability (> 3 V) such as non-aqueous electrolytes or ionic liquids are used to enhance the specific energy of the capacitor while high specific power is achieved by employing aqueous electrolytes of high ionic conductivity [13]. Carbon-based materials are extensively investigated as electrode materials for EDLCs due to their huge surface area (> 1500 m² g⁻¹), high conductivity, relatively low cost, high chemical stability, and well-established electrochemistry. Besides they are available in different forms such as activated carbons, carbon aerogels, carbon nanotubes, carbon fibers, etc. [14]. Even though a specific surface area of carbon materials is considered as an important parameter to maximize the specific power and energy, recent research on hierarchical porous carbon has revealed that tailoring the size, geometry and ratio of different sized pores are crucial to achieving high power rate capability [6,15]. Indeed, micropores enhance the specific gravimetric capacitance remarkably due to space confinement effect enrich the charge density by the restricted entry of solvent sheath into the micro pores. Or else the formation of secondary adsorption layer of electrolyte dilutes the energy density of adsorbed ions. But the sluggish diffusion of ions into the micro pores due to strong ion-ion interaction as well as overflowing of an electrolyte at higher current rate reverse the trend and limits the power rate capability of the capacitor. It is obvious that the presence of meso pores along with micro pores is

* Corresponding author.

E-mail address: michaelm@ssn.edu.in (M.S. Michael).

essential to facilitate the diffusion of ions inside micro pores by providing the connectivity hence hierarchical porous carbon electrode with the appropriate ratio of meso and micro pores are preferred to develop high powered supercapacitor.

Generally, the concept of hybridization of electrodes of two different storage mechanisms is adapted to improve the energy density of the capacitor by widening the potential window as well as charge transfer across the electrode/electrolyte interface of the pseudo capacitive electrode. However, the hybridization concept is never tried to overcome the poor power performance of the micro porous electrode. In the present work, we study the influence of hybridization of different storage mechanisms on the power rate capability of the microporous electrode. The significant improvement of power rate capability of hybrid capacitor demonstrates that the substitution of one of the microporous electrodes with nanostructured pseudocapacitive electrode could minimize the influence of space confinement on power capability. Moreover uniform sized microporous Activated Carbon (mAC) is coupled with the nanostructured pseudo capacitive material, MnCo_2O_4 and the capacitive performance of hybrid capacitor are compared with that of the symmetric capacitor.

It is challenging to get the pores of uniform size without the help of template since most of the activation methods lead to broad pore size distribution with a combination of micro, meso and macro pores. The present work shows our success in generating micro pores of narrow distribution, $< 1 \text{ nm}$ by controlled chemical activation using KOH. The systematic study on the capacitive performance of the mAC in symmetric and hybrid configuration employing different aqueous solutions, namely acidic ($0.5 \text{ M H}_2\text{SO}_4$), alkaline (2 M KOH) and neutral (1 M KCl) as well as in non-aqueous electrolyte (1 M TEA-BF_4 in 1:1 DC & EC) reveals that coupling of mAC with pseudocapacitive binary metal oxide, MnCo_2O_4 in hybrid configuration resolve the poor power performance issue of mAC significantly.

2. Materials and methods

2.1. Activation of petcoke

Commercial petcoke (Graphite India Ltd., Kolkata) was activated by KOH according to the process schematic illustrated in Fig. 1. 1 g of petcoke was impregnated in 100 ml aqueous solution of 5 M KOH (Merck) overnight. The mixture was then dried at 100°C to remove the moisture, activated at 750°C at the heating rate of 5°C min^{-1} and annealed at the same temperature for 2 h under Ar atmosphere. After cooling, the activated carbon was washed intensively with water to remove the last trace of KOH.

2.2. Synthesis of MnCo_2O_4

Single phase nanosized MnCo_2O_4 powder sample was synthesized from their metal acetates by adapting a simple solution synthesis protocol involving acetyl acetone as a complexing agent and cetyl alcohol as a dispersing agent. Stoichiometric quantities of the above starting materials were dissolved in the appropriate quantity of de-ionized water/isopropanol mixtures (4:1 ratio) separately and mixed thoroughly using an ultrasonic processor (UP200S 200 watts, 40 kHz Hielscher Ultrasonics GmbH, Germany) for 30 min. The resulting dark-colored clear solution was continuously stirred at 110°C to facilitate the evaporation of water until sticky gel-like substance was obtained. The gel-type precursor was heated to 650°C at the heating rate of 5°C min^{-1} under a flowing pure argon atmosphere and annealed at the same temperature for 6 h in a programmable tubular furnace (CY-T1200, CY scientific instrument Co., Ltd). When the programmed time was over, the sample was automatically cooled down to room temperature in the atmosphere of argon gas control the morphology and texture of nano particles.

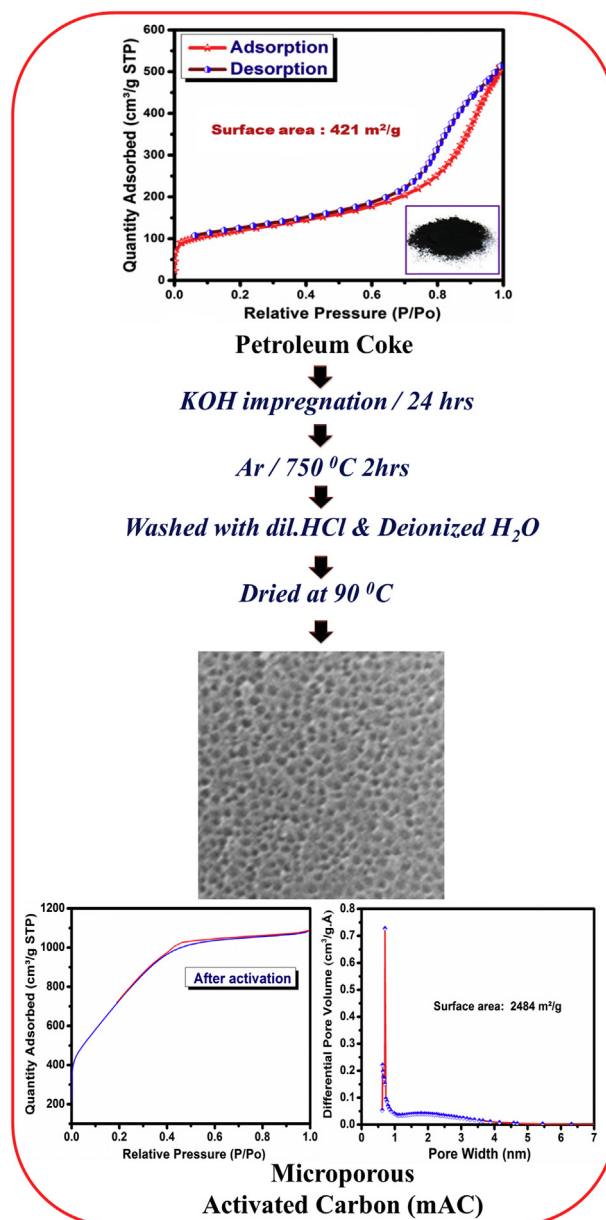


Fig. 1. Schematic illustration of activation of petcoke by chemical impregnation method.

2.3. Characterization of materials

The X-ray diffraction (XRD) pattern of synthesized MnCo_2O_4 was recorded on Bruker D2 Phaser desktop X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$) as the X-ray source. N_2 adsorption-desorption isotherm was studied by employing Micromeritics ASAP 2020 sorption analyzer. Prior to analysis, the samples were degassed for 3 h at 300°C under vacuum ($10\text{--}5 \text{ mbar}$) in the degassing port of the adsorption analyzer. The specific surface area was deduced from Brunauer-Emmett-Teller (BET) analysis and the pore size distribution was calculated using Barrett-Joyner-Halenda (BJH) method. The FT-IR spectra were recorded using Perkin Elmer FT-IR spectrometer using Attenuated total reflection (ATR) technique. The sample was scanned in the range of $4000\text{--}400 \text{ cm}^{-1}$. The surface morphology of mAC was analyzed by FESEM using Carl Zeiss SUPRA-55 microscope.

Download English Version:

<https://daneshyari.com/en/article/7744263>

Download Persian Version:

<https://daneshyari.com/article/7744263>

[Daneshyari.com](https://daneshyari.com)