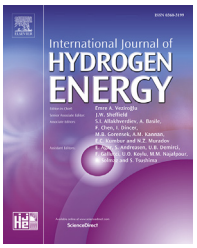
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–8

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Supercapacitive properties of activated carbon electrode using ammonium based proton conducting electrolytes

Sindhuja Manoharan [a], *Surjit Sahoo* [a], *Parthiban Pazhamalai* [a], *Sang Jae Kim* [a,b,*]

[a] *Nanomaterials and System Laboratory, Department of Mechatronics Engineering, Jeju National University, Jeju 63243, South Korea*

[b] *Department of Advanced Convergence Technology & Science, Jeju National University, Jeju 63243, South Korea*

ARTICLE INFO

Article history:
Received 27 September 2017
Received in revised form
11 November 2017
Accepted 21 November 2017
Available online xxx

Keywords:
Proton conducting electrolytes
Activated carbon
Cyclic voltammetry
Nyquist plot
Bode phase angle plot

ABSTRACT

In this study, we demonstrated the usefulness of proton conducting electrolytes (such as ammonium thiocyanate (NH_4SCN) and ammonium nitrate (NH_4NO_3)) for electrochemical energy storage devices using activated carbon (AC) as the electrode material. The cyclic voltammetry analysis revealed the presence of rectangular shaped cyclic voltammograms indicating the presence of electrical double layer capacitance in AC electrode using NH_4SCN and NH_4NO_3 electrolytes. The mechanism of charge-storage in AC electrode using the proton conducting electrolytes has been studied in detail using electrochemical impedance spectroscopy (Nyquist and Bode plots). The galvanostatic charge-discharge analysis revealed that a maximum specific capacitance of AC electrode using NH_4SCN and NH_4NO_3 electrolytes was found to be 136.75 mF cm^{-2} and 113.38 mF cm^{-2} at a current density of 0.5 mA cm^{-2}. This study would open a new avenue for the use of ammonium based proton conducting electrolytes for supercapacitor applications.

Introduction

The prime research on energy storage is being a major concern because of its booming threat to the human society [1]. As the utilization of energy is at a faster rate than the available resources, even though the rate of consumption could not be reduced the only solution being is the increase in efficiency with a responsibility of eco-friendly devices for energy storage applications is the ultimate and primary focus of research in the present scenario [2]. Of the energy storage devices, supercapacitors are being widely under research because of its advantages of high power density though the energy density increment is also being under research as it could be the most opted storage devices because of its ultra-fast charging [3]. To make an effective supercapacitor, understanding the role of electrode and electrolyte is very important [4]. The charge storage mechanism is either by electric double layer capacitance and/or faradaic capacitance [5–7]. The aqueous electrolytes are advantageous for its high safety because of its non-flammability, low manufacturing cost as it does not need any special procedures for the

* *Corresponding author*. Nanomaterials and System Laboratory, Department of Mechatronics Engineering, Jeju National University, Jeju 63243, South Korea.
E-mail address: kimsangj@jejunu.ac.kr (S.J. Kim).

https://doi.org/10.1016/j.ijhydene.2017.11.121
0360-3199/

fabrication [8]. Both the electrolyte and electrode plays a vital role in the energy storage performance of a supercapacitor device since the former offers the ions and the later provides the electrostatic potential which results in the synergetic interaction between the electrochemical ions at the electrode surface [9,10]. The aqueous electrolytes limit the potential window to 1.23 V due to the dissociation of water, though practically the potential window limits to less than 1 V [11]. Generally, the electrochemical performance of active material is strongly influenced by the electrolyte. For an ideal electrolyte in the electrochemical devices, it should possess a high ionic conductivity, high chemical, electrochemical stability and excellent temperature stability [12]. The concept of electric double layer capacitance is obtained with the Helmholtz inner and the outer plane where the diffusion occurred at the Helmholtz outer plane [13]. Then, the solvated ions in the electrolyte being attracted by the charged electrode, crossing the bulk solution, diffusion layer, diffusive layer and stored at the interface of electrode/electrolyte [9]. Theoretically the concentrated electrolytic solution possesses the charge separation in the order of few Å and in diluted solutions the diffusive part of a double layer composing of Helmholtz outer and inner plane as calculated to be around 1000 Å and higher surface area and concentration of the electrolyte – higher the capacitance value [9]. The electrolytic solution in electrochemical capacitor is indeed a source of ions stored in the electric double layer formed at the electrode/electrolyte interface [14,15].

The interaction of electrolyte and electrode are being complex to study once resolved, it could be a greater leap in the supercapacitor applications [16]. Proton conducting electrolytes researches in supercapacitors are at a very budding stage, a lot of explorations needed to be done for the better understanding [12,17]. The proton has the high mobility compared to any other electrolyte ions in the aqueous medium [18,19]. Recently proton conducting electrolytes which are widely used in fuel cells are examined for the supercapacitor applications [20]. Several proton conducting electrolytes such as H_2SO_4, H_3PO_4, heteropolyacids (such as silico/molybdo/phospho tungstic acids) are examined as novel electrolytes for supercapacitors during this decade [20–22]. In this regard, ammonium based proton conducting electrolytes are examined for energy storage applications. On the other hand, ammonium based electrolytes such as ammonium thiocyanate (NH_4SCN) and ammonium nitrate (NH_4NO_3) shows to be promising mainly of their good ionic conductivity with excellent redox chemistry of SCN groups which can mimic the similar role of redox additive electrolytes in supercapacitors [23]. The ammonium based solid proton conducting electrolytes are widely used in fuel cell applications [24,25]. Both NH_4SCN and NH_4NO_3 are classified as less hazardous materials and this provides evidences for the environmentally safe and stable use [23]. However, NH_4SCN is weakly acidic, NH_4NO_3 is a neutral electrolyte and we have made a comparison of the proton conducting electrolytes for electrochemical devices [26–29]. In this study, we examined the supercapacitive properties of activated carbon (AC) electrode using two proton conducting electrolytes for energy storage application.

Experimental section

Materials and methods

Activated carbon (AC), N-methyl pyrrolidone, NH_4SCN, and NH_4NO_3 are purchased from the Daejung chemical Ltd., South Korea. Polyvinylidene difluoride (PVDF) was purchased from Sigma Aldrich Ltd., South Korea. All the chemicals used in this experiment were of research grade.

Materials characterization

X-Ray diffraction (XRD) analysis was performed with X-ray diffractometer system (D/MAX 2200H, Bede 200, Rigaku Instruments C) operated at 40 KV/40 mA with Cu – K_α radiation. The diffraction pattern was recorded 2θ from 5° to 80° with a scan rate of 0.02°. The Raman spectra of the samples were studied using a LabRam HR evolution Raman spectrometer (Horiba Jobin-Yvon, France). The Raman spectrum was obtained with 514 nm wavelength of an Ar^+ ion laser. The surface morphology of the AC electrodes was examined using Field emission-scanning electron microscope (JSM-6700F, JEOL Ltd.). The N_2 adsorption-desorption isotherms of the AC powder was measured at 77 K using a NOVA 2000 system (Quantachrome, USA) and the pore size distribution was calculated using Horvath-Kawazoe (HK) method.

Electrochemical analysis

The working electrode AC was prepared using slurry coating method as reported in our earlier work. Briefly, AC and binder (PVDF) were mixed in the ratio of 95:5 using N-Methyl pyrrolidone as a dispersant and grounded well until a homogeneous slurry was obtained. After that the slurry was casted on the surface of stainless steel current collector (1×1 cm^2) and allowed to dry at 60 °C for overnight in a hot air oven. 1 M solution of proton conducting electrolytes (NH_4SCN and NH_4NO_3) were used in this work. The electrochemical properties of the AC electrode were evaluated using a three-electrode configuration (Platinum as counter electrode, Ag/AgCl as reference electrode and AC as working electrode). The electrochemical characterization with cyclic voltammetry (CV) obtained using different scan rates (5–100 mV s^{-1}) and galvanostatic charge discharge (CD) measured using different current densities (0.5–5 mA cm^{-2}) and electrochemical impedance analysis EIS were carried out on Autolab PGSTAT302 N electrochemical workstation. The specific capacitance (C_{sp}) of the AC electrode was obtained from the CV profiles using the relation [30]:

$$C_{sp} = \left[\left(\int I\,dV\right) \Big/ (S \times \Delta V \times A)\right] \text{F cm}^{-2} \quad (1)$$

Here, "$\int IdV$" is the integral area of one complete cycle of CV curve, "A" is the area of the active material, "S" is the scan rate, and "ΔV" is the potential window. The specific capacitance (C_{sp}) of the AC electrode was obtained from the CD profiles using the relation [30]:

$$C_{sp} = [(I \times \Delta t)/(\Delta V \times A)] \text{ F cm}^{-2} \quad (2)$$

Please cite this article in press as: Manoharan S, et al., Supercapacitive properties of activated carbon electrode using ammonium based proton conducting electrolytes, International Journal of Hydrogen Energy (2017), https://doi.org/10.1016/j.ijhydene.2017.11.121