



Electrochemical properties of solid leather wastes based supercapacitor electrodes using H₂SO₄ electrolyte



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ABSTRACT

Solid leather wastes (SLW) based porous carbons were used as the electrode material for supercapacitors in acid (H₂SO₄) medium. Electrochemical investigations indicate that samples activated at 900 °C shows a maximum capacitance of 1833 F/g at a scan rate of 1 mV/s in 1 M H₂SO₄ electrolyte. Moreover, SLW porous carbon electrodes show excellent cycling stability over 500 cycles at a constant current density of 20 A/g. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) studies propose porous carbons developed from SLW could be an excellent electrode material for supercapacitors even in strong acid electrolyte medium.

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1. Introduction

Nowadays worldwide growing energy demand has initiated the exploration of new energy systems. Among them, supercapacitors paid much attention due to their high power density, excellent cycling stability, low cost, fast charge–discharge rate and environmental friendliness [1,2]. Even though the energy storage capacity of a supercapacitor depends on the effective surface area and tunable porous structure of the electrode material; electrolytes also play vital role establishing superior performance [3,4]. Electrolytes influence the major parameters such as power density, potential window, internal resistance, ionic conductivity, operating temperature range, cyclic stability, rate performance, environmental friendliness and self discharge in both electric double layer and pseudocapacitors [5].

Aqueous electrolytes are more favorable among other liquid electrolytes due to their low cost, comparatively higher ionic conductivity and can be handled easily during fabrication and assembling process [5]. Selection of aqueous electrolytes relies on the size of the anions and cations and their mobility's. From the earlier reports it is observed that specific capacitance is directly proportional to ionic conductivity of the electrolytes [5,7]. 1 M H₂SO₄ acid electrolyte medium exhibits high ionic conductivity of 0.8 S cm⁻² at 25 °C which is one order magnitude higher than organic and ionic liquid electrolytes that could be beneficial for lowering the

equivalent series resistance (ESR) value and better power delivery [5,6].

Electrochemical studies of SLW have already been reported by our previous works using KOH and KCl [8,9]. However the present work is focused to study the electrochemical behavior of the SLW in the presence of strong acidic electrolyte medium like H₂SO₄, looking into the beneficial aspects of acid electrolyte medium and its role in double layer formation. Hence the present study is focused to explain the potential of SLW in 1 M H₂SO₄ for charge storage using cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques.

2. Experimental

Porous carbons were prepared in the laboratory using the dried solid leather wastes (SLW) obtained during “leather crusting process” as the precursor material by two-stage process: precarbonization and chemical activation as reported in our previous literatures [8,9,10]. In brief, precarbonized crust leather carbon (CPC) was prepared by heating SLW at 400 °C (heating rate of 5 °C min⁻¹) and soaking at the same temperature for about 4 h. CPC is then subjected to chemical activation with aqueous solution of KOH. The ratio of KOH/precarbonized carbon was screened and fixed at 4. After mixing the chemical activator and precarbonized carbon, the slurry was dried under vacuum at 110 °C for 1 h. Samples were then activated in a furnace at temperatures 600, 700, 800 and 900 °C (a heating rate of 5 °C min⁻¹), maintained at the same

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temperature for 2 h and the resultant samples were labelled as CPC-6, CPC-7, CPC-8 and CPC-9 respectively. Supercapacitor electrodes were prepared by mixing 95 wt.% porous carbons and 5 wt.% nafion to form a paste and coated onto the nickel foam. The coated electrode was dried at 70 °C in an oven for 2 h. The typical mass of the electrode material was found to be 0.5 mg.

Surface morphology were observed using Hitachi S – 4800 high resolution scanning electron microscope. High resolution transmission electron microscope (HR-TEM) supplied by JEOL 3010 instrument was employed for viewing the microstructure of the porous carbons. The electrochemical characterizations of samples were done in electrochemical impedance analyzer PARSTAT-4000 with in 1 M H₂SO₄ as electrolyte at room temperature with three electrode configuration. The carbon coated on the nickel foam, Ag/AgCl and platinum wire were used as the working, reference and counter electrode, respectively. The specific capacitance of carbon electrode can be calculated from the cyclic voltammograms according to the following formula [11],

$$C_{sp} = \frac{1}{vm(V - V_0)} \int_{V_0}^V I(V)dV \quad (1)$$

where C_{sp} is the specific capacitance (F/g), is a current response in accordance with the sweep voltage (A), v is the potential scan rate (V/s), $V - V_0$ is the potential window (V) and m is the mass of the electrode in grams.

3. Results and discussion

Scanning electron micrograph of CPC in Fig. 1a shows that the surface is fibrous in nature without any pores. Since the precarbonization temperature was insufficient enough to remove the volatile components and to create porosity. In contrast KOH activated carbon CPC-9 (Fig. 1b) displays well-established pores on their surface due to removal of non-carbonaceous materials by

the mutual effect of the activation agents and the temperature employed. Amorphous nature of the precarbonized carbon samples were established in the HR-TEM images of CPC in Fig. 1c, while both amorphous and crystalline nature were detected in CPC-9 as shown in the Fig. 1d. Additionally, selected area electron diffraction (SAED) pattern for CPC-9 (inset of Fig. 1d) shows the interlayer distance 0.3522 nm corresponding to (0 0 2) plane of graphite. XRD pattern reported in our previous papers confirms the graphitic structure and matches with JCPDS card number 75-2078 [8,10].

The supercapacitive properties of the SLW derived carbons were determined using cyclic voltammetry studies performed at room temperature within the scan rate range of 1–500 mVs⁻¹ in 1 M H₂SO₄ (Fig. 2a). The shape of the voltammograms for CPC, CPC-6, CPC-7, and CPC-8 are rectangular representing a typical voltammogram for supercapacitors. The CV curves for CPC-9 exhibits a leaf like shape without any redox peaks indicating that charge storage mechanism is purely electrostatic. The highest C_{sp} value 1833 F/g is obtained for CPC-9 at a scan rate of 1 mV/s using equation. The tilting of cycle voltammograms in porous carbon samples could not be assigned to the oxygen functional groups, but shall be due to the electrode and electrolyte resistances. It is observed that specific capacitance (C_{sp}) increases with a decrease in scan rate for all the carbon samples, which is due to the fact that at a low scanning rate, there is adequate time for ions to diffuse into the inner pores of the electrodes, this is essential for the formation of electric double layers [Fig. 2b]. Hence, more ions are adsorbed on the surface of the electrode, which is associated with a better capacitive behavior.

A symmetrical triangle galvanostatic charge-discharge (GCD) curve reflects ideal supercapacitive behavior with high electrochemical stability. Here we discuss on the charge discharge effects of CPC-9 which got exceptionally high values of specific capacitance comparing to other porous carbon electrodes. Inset of Fig. 3a shows the GCD curves of CPC-9 in 1 M H₂SO₄ and curves are almost symmetrical triangular in nature. The long term cycling

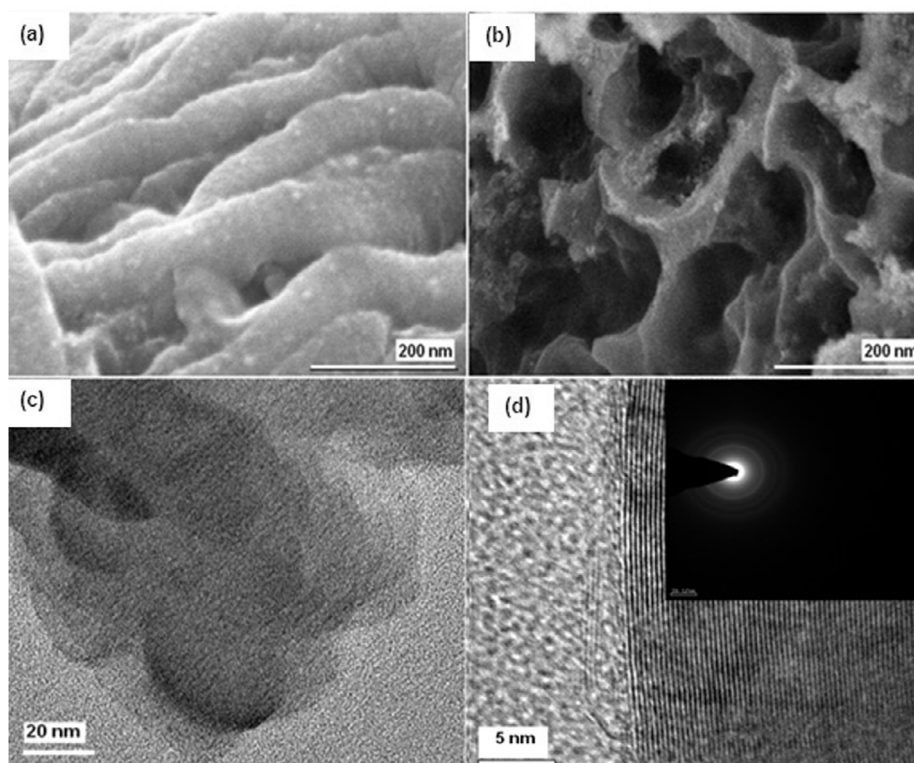


Fig. 1. a and b. SEM images of CPC and CPC-9. c and d. HR-TEM images of CPC and CPC-9, [Inset of figure d-Selected area electron diffraction (SAED) pattern for CPC-9].

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