

Correlation of energy storage performance of supercapacitor with *iso*-propanol improved wettability of aqueous electrolyte on activated carbon electrodes of various apparent densities



Denys G. Gromadskyi^a, Jung H. Chae^a, Stuart A. Norman^b, George Z. Chen^{a,c,*}

^a Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, Nottingham NG7 2RD, UK

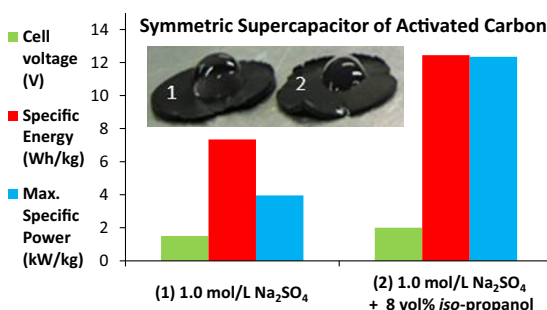
^b E.ON Technology Centre, Ratcliffe on Soar, Nottinghamshire NG11 0EE, UK

^c Department of Chemical and Environmental Engineering, and Centre for Sustainable Energy Technologies, Faculty of Science and Engineering, University of Nottingham Ningbo China, Ningbo 315100, PR China

HIGHLIGHTS

- *Iso*-propanol improves wettability of aqueous electrolyte on activated carbon.
- *Iso*-propanol in aqueous electrolyte affects charge storage in porous carbon.
- Apparent carbon density changes storage behaviour in presence of *iso*-propanol.
- Improved energy storage performance is achieved in aqueous supercapacitors.
- A pore-ion-solvent model is proposed to explain the mechanism of improvement.

GRAPHICAL ABSTRACT



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ABSTRACT

Addition of *iso*-propanol in the aqueous electrolyte of 1.0 mol/L Na₂SO₄ was found to be most effective at about 8 vol.% to minimise electrolyte surface tension, and hence maximise electrolyte wetting on a commercial supercapacitor grade activated carbon powder. The wetting improvement was further studied on die-pressed cylindrical thin pellets of polytetrafluoroethylene bonded activated carbon powder at three different apparent densities (0.70, 0.55 and 0.35 g/cm³) using adsorption isotherm, cyclic voltammetry and electrochemical impedance spectroscopy. Enhanced charge storage performance of the activated carbon at 0.70 and 0.55 g/cm³ in apparent density was observed in electrolyte containing *iso*-propanol. The effect of *iso*-propanol became more prominent at high polarisation potentials. However, at the lowest density (0.35 g/cm³) studied, the capacitance decreased in the presence of *iso*-propanol, which can be attributed to the *iso*-propanol molecules entering the nano-pores of the activated carbon particles. In symmetrical supercapacitors with the dense activated carbon electrodes, addition of *iso*-propanol to the aqueous electrolyte increased the cell voltage, specific energy and maximum specific power from 1.5 to 2.0 V, 7.34 to 12.44 W h/kg, and 3.96 to 12.35 kW/kg, respectively, under comparable conditions.

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* Corresponding author at: Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, Nottingham NG7 2RD, UK.
E-mail address: george.chen@nottingham.ac.uk (G.Z. Chen).

1. Introduction

Supercapacitors (SCs) are relatively new energy (electricity) storage devices with high power density and long cyclic life, and can offer great flexibility and modularity for a wide range of mobile, stationary, distributed and centralised applications such as hybrid electric vehicles [1] and wind turbines for power generation [2]. These characteristics of SCs are highly desirable for development of highly efficient and low carbon emission energy technologies in the post-fossil era of human civilisation. Initially, symmetrical SCs were developed with the same and equal amounts of electrode material, e.g. activated carbon (AC). They are also known as electrochemical double layer capacitor (EDLCs), because an electrical double layer is formed on the electrode/electrolyte interface between ions and oppositely charged surface [3,4]. This type of SCs has significantly higher power density, but their energy storage capacity is inferior to conventional rechargeable batteries [5]. Recently, asymmetrical designs (or supercapacitors) [6] that combine properties of electrodes of both the EDLC and battery to improve energy density have been suggested (e.g. AC/Li-graphite [7], AC/Ni(OH)₂ [8], AC/MnO₂ [9] and others [10–12]), although such changes require a careful balance of resources and costs [13].

SCs can use an organic [14,15], aqueous [16,17], or ionic liquid [18,19] electrolyte. In comparison to their aqueous counterparts, organic electrolytes have wide potential windows, often above 2.5 V. This feature of organic electrolytes is a great advantage since the maximum operating voltage of the EDLCs cannot be greater than the electrolyte decomposition voltage. On the contrary, the water decomposition voltage is 1.229 V at pH 7 according to the Pourbaix diagram [20].

However, a number of recent studies have claimed that the use of aqueous electrolytes does not necessarily lead to a small operating voltage. Upon appropriate selection of electrode materials the overpotentials of hydrogen and/or oxygen gas evolution can significantly increase. Hence, noticeably greater voltages of 1.7–2.2 V in neutral aqueous electrolytes can be achieved, particularly if the capacitances of the two electrodes are appropriately unequalled [21–24]. Of the various inorganic salts used in aqueous electrolytes, alkali metal sulphates are more favourable because both the alkali metal and sulphate ions are electrochemically inert in water. Conductivities of alkali metal sulphate solutions are determined largely by the hydration of alkali metal ions and follow the order of $K^+ > Na^+ > Li^+$ [25]. Nonetheless, Na₂SO₄ is still more preferable because of its higher solubility in water (about 20 g/100 g H₂O at 20 °C as compared with 12 g/100 g H₂O for K₂SO₄) [26]. The optimal concentration of such an electrolyte has also been studied and found to be about 1.0 mol/L. The solubility of a salt is directly related to the ionic conductivity of the electrolyte which in turn affects the power performance of the SC. Specially, on the same RC-time scale (for charging and discharging an SC of resistance, R, and capacitance, C), the attainable specific capacitance would decrease if interactions between ions become too strong, because the mobility of the ion decreases in this case, so does the ionic conductivity [27].

When using an aqueous electrolyte and a carbon electrode, impregnation of the electrolyte into the electrode becomes an issue because carbon materials are mainly hydrophobic by nature. Therefore, they adsorb non-polar molecules better than the polar ones [28–30]. By inclusion of heteroatoms (O, N) in the carbon structure, its hydrophilic properties can be improved [31] to some degree. Using a hydrophobic binder, e.g. polytetrafluoroethylene (PTFE) [32], gives improved adhesion and cohesion of carbon particles [33], but also increases the surface tension, which in turn reduces and/or slows the impregnation of the aqueous electrolyte

into the carbon structure. For large scale manufacturing, the slow electrolyte filling process in the fabrication of SCs could also be problematic. Therefore, this study was undertaken to better understand and intentionally resolve the problems mentioned above. One of the direct approaches is to add an amphiphilic agent, such as an alcohol, to improve the wettability of the aqueous electrolyte to the PTFE bonded AC powder. It is desirable that the alcohol should have a relatively low vapour pressure to avoid evaporation during fabrication and operation of the SC. In addition, it has been reported that the reduction of electrolyte surface tension became more prominent in the order of methanol < ethanol < propanol [34]. The rate of alcohol adsorption by AC was also found to increase in this order [35]. In other cases [36,37], surfactants of large molecules were used to improve electrolyte wetting, including sodium dodecyl sulphate, polyethylene glycol, and *p*-*t*-octylphenol (Triton X-100) which however causes complication in charge conduction and storage mechanism. Based on these considerations, *iso*-propanol was selected for the purposes of this study.

2. Experimental

2.1. Chemicals, materials and electrode fabrication

Commercially available activated carbons (ACs) can vary significantly in structure, surface functionalities, and electrochemical properties. For supercapacitor applications, not all types of ACs are suitable. One of the important reasons is that the intrinsic electronic conductivity of an AC decreases with increasing the porosity. However, a more porous structure is generally beneficial to increasing the ionic conductivity. In this work, a relatively unique supercapacitor grade commercial product of AC (YP50F, Kuraray Chemical Co.) was studied for its material properties in relation to electrolyte wetting and performance in laboratory SCs.

For electrochemical studies, the AC powder was made into pellet type electrodes by firstly mixing with polytetrafluoroethylene (PTFE) as a binder (60 wt.% aqueous dispersion, Sigma Aldrich) to an AC/PTFE mass ratio of 19:1. Ethanol was then added (10 mL/g-AC) to disperse the AC-PTFE mixture into a homogeneous slurry [33]. During mixing, ethanol evaporated gradually, leading to a thick paste which was then die-pressed into thin cylindrical pellets (1.3 cm diameter). By changing the pressure (2–6 t/cm²), pellets of different apparent densities were produced according to the weight (*ca.* 0.05 g) and dimensions of the pellets (0.35 ± 0.02, 0.55 ± 0.02 and 0.70 ± 0.02 g/cm³). Finally, the pellets were vacuum dried for 4 h at 100 °C before testing.

2.2. Physical analyses

The pore size and volume distribution of the AC samples were determined from the nitrogen adsorption/desorption isotherms at 77 K (ASAP 2420) by applying the density function theory (DFT) which is regarded to be more suitable for analysis of porous materials in which large micro- and small mesopores (*i.e.* supermicropores) prevail [38], instead of the conventional Brunauer–Emmett–Teller (BET) or Barrett–Joyner–Halenda (BJH) methods [39–41]. Precisely such materials are more preferred for use in carbon based EDLCs [42].

Sample morphology was investigated by scanning electron microscopy (SEM, Philips FEI XL30 FEG-ESEM). Surface tension was measured using the stalagmometric method at 20 °C with distilled water as the standard reference. The capillary diameter of the stalagmometer was 0.34 mm. The surface tensions (σ) of the solution of interest can be calculated by the following equation [43],

$$\sigma \approx \sigma_0 \frac{n_0 \rho}{n \rho_0} \quad (1)$$

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