



# A high-voltage asymmetric electrical double-layer capacitors using propylene carbonate

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## ABSTRACT

The upper limit of the double-layer potential window for the propylene carbonate/carbon black interface is effectively extended from 0.1 to 1 V (vs. Ag/AgNO<sub>3</sub>), compared with activated carbon. Commercial carbon black with low defects and activated carbon are respectively employed as positive and negative electrode materials to construct an advanced asymmetric supercapacitor with cell voltage reaching 3 V in propylene carbonate. This asymmetric supercapacitor of the double-layer type with a cell voltage of 3 V is very stable in 10,000-cycle charge-discharge tests.

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## 1. Introduction

Electrochemical capacitors (ECs) or supercapacitors (SCs) are typical energy storage devices of superior capabilities in high-rate charge-discharge and long cycle life compared to rechargeable batteries [1,2]. Commonly, ECs provide the advantages of environmental friendliness, high safety, good reliability, low cost, etc. [3]. Among ECs, electrical double-layer capacitors (EDLCs) utilize arranged ions/polar solvents for charge storage under applied electric fields [4]. Redox SCs provide pseudo-capacitance via superficial redox couples [5]. Asymmetric SCs (ASCs) consist of two dissimilar materials with complementary potential windows to enlarge the cell voltage [6]. Although ASCs of large cell voltages raise the specific energy effectively, the energy density of ECs is much lower than that of rechargeable batteries and fuel cells [7,8]. Moreover, the high-rate charge-discharge performances of ASCs can be maintained using electrode materials of double-layer type in one of the dissimilar materials [9].

Practically, activated carbons (ACs) are utilized to obtain high specific capacitance ( $S_{CT}$ ) due to their high specific surface area accessible to electrolyte for double-layer charge storage/delivery. Moreover, organic electrolytes such as acetonitrile and propylene carbonate (PC) are widely used to enlarge the cell voltage for organic EDLCs of relatively high energy density (in comparison with aqueous SCs). Unfortunately, rich oxygen-containing functional groups are formed on the surface of ACs with extensive pores. Furthermore, residual water within ACs is

an unavoidable issue because of the hydrophilic and micro-porous characteristics of ACs containing oxygen-functional groups [10]. These functional groups and residual water react with organic electrolytes when ACs are operated at potentials negative/equal to 1.5 V or positive/equal to 4.5 V against Li/Li<sup>+</sup> [11]. The gas generation from electrolyte decomposition and the presence of solid-electrolyte-interface-like films on the electrode surface significantly raise the cell resistance and probably decrease  $S_{CT}$  of resultant devices [12,13]. Hence, a complicated procedure is applied to dry AC-coated electrodes to reach a cell voltage of 2.5–2.7 V, which commonly consumes 30–40% cost although the above cell voltages are insufficient.

Carbon-based EDLCs have been commercialized for quite a long time because of their abundance, low cost, high-electrolyte accessibility, and good electrical conductivity [14]. Commercially available carbon blacks (CBs) are nano-sized particles with a diameter of around 10 nm and commonly employed to reduce resistance of oxide-based electrodes for energy-storage/-conversion devices [16]. Accordingly, CBs with high conductivity have been applied in aqueous and organic electrolyte-based EDLCs [17]. Recently, CBs were found not to cause electrolyte decomposition when they were added into ACs as conductive additives under the high-voltage operation [18]. Moreover, the simple drying process of CB-based electrodes is very attractive to organic EDLCs. Therefore, CBs are considered a promising electrode material of high-voltage organic ASCs.

We demonstrate a new ASC consisting of CB-coated and AC-coated electrodes which were simply dried at 85 °C for 2 h, which utilizes the double-layer charge storage mechanism with enlarged cell voltage. Here, CBs with low defects but relatively high specific surface area

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effectively extend the upper limit of working potential window from 0.1 to 1 V (vs. Ag/AgNO<sub>3</sub>), compared with the AC-coated electrode. This advanced 3-V ASC employs commercial CB-coated and AC-coated electrodes as positive and negative electrodes, respectively.

## 2. Experimental

Commercial CBs (UniRegion Bio-Tech, Taiwan; specific surface area ( $S_{\text{BET}}$ ): 472 m<sup>2</sup> g<sup>-1</sup>) and ACs (ACS-679, China Steel Chemical Corporation, Taiwan;  $S_{\text{BET}}$ : 1635 m<sup>2</sup> g<sup>-1</sup>) were uniformly mixed with polyvinylidene difluoride (10 wt%) and N-methyl pyrrolidinone for 30 min. The slurry was coated onto a carbon-coated aluminum electrode (Eternal Materials Co, Ltd.) and simply dried at 85 °C for 2 h to form the working electrode under the three-electrode mode. A platinum helix and an Ag/AgNO<sub>3</sub> electrode (Argenthal, 0.01 M AgNO<sub>3</sub>, 0.1 M (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NClO<sub>4</sub> in AN) were used as the counter and reference electrodes, respectively. The electrolyte is a 1-M tetraethyl ammonium tetrafluoroborate (TEABF<sub>4</sub>) PC solution in a beaker cell. For the two-electrode mode, the asymmetric cell consisted of CB-coated and AC-coated electrodes without any separator.

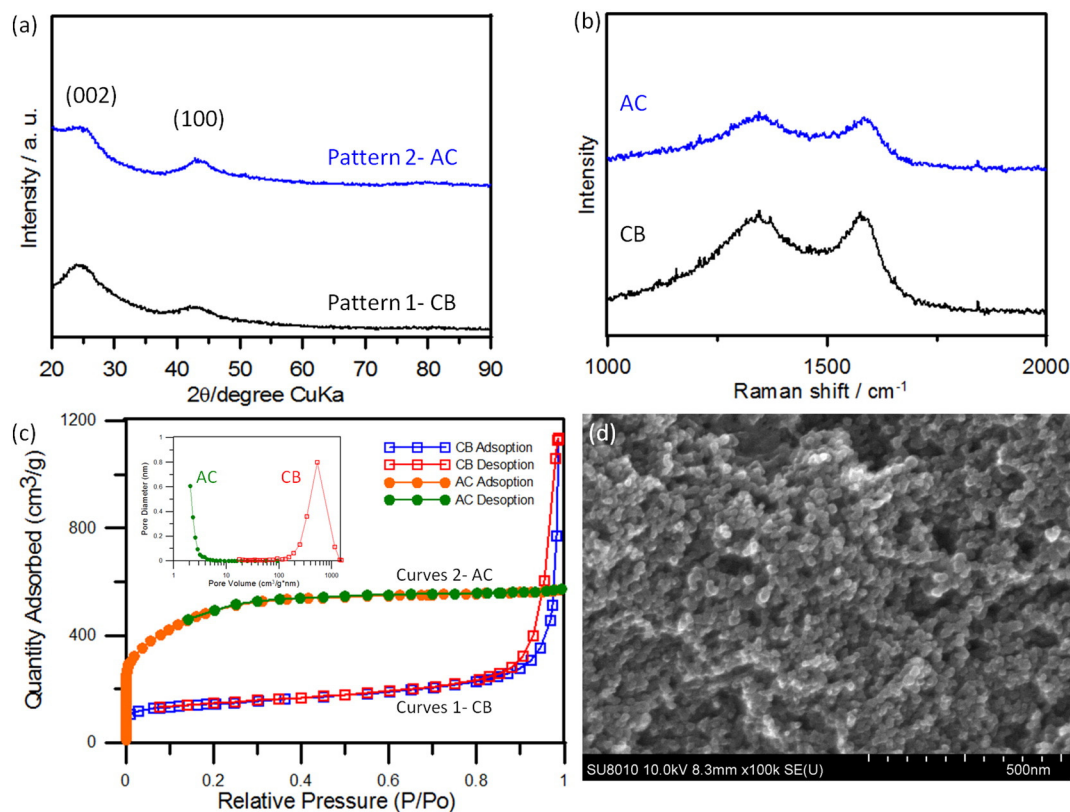
The electrochemical characteristics were examined by an electrochemical analyzer system, CHI 760E (CH instruments, USA), under both three-electrode and two-electrode modes using cyclic voltammetry (CV) and chronopotentiometry. The electrochemical characteristics of ACs in the standard PC electrolyte were examined between −0.6 (open-circuit potential,  $E_{\text{OCP}}$ ) and 1.4 V. The cell voltage of full cells is from 0 to 3 V. All electrochemical tests were conducted in a nitrogen-filled glove box (MBRAUN, Germany) containing <1 ppm H<sub>2</sub>O and O<sub>2</sub>. The crystalline structure of CB was characterized by X-ray diffraction (XRD, Bruker) with Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). The surface morphology of CB was examined by a field-emission scanning electron microscope (FE-SEM, Hitachi SU8010) and a FE transmission

electron microscope (ULTRA-HRTEM, JEM-ARM200FTH). Nitrogen adsorption-desorption isotherms were collected at 77 K utilizing Micromeritics 2020 analyzer (USA). The Brunauer-Emmett-Teller (BET) method was employed to calculate  $S_{\text{BET}}$  using adsorption data collected in a relative pressure range of 0.02–0.2. The non-local density functional theory (NLDFT) and Monte-Carlo methods were utilized to obtain the pore size distribution of a material with micro-pores (<2 nm) and meso-pores (2–50 nm). Raman spectra were conducted by a Raman microscope (Thermo DXR-HR, HORIBA) using the 532-nm laser. X-ray photoelectron spectroscopic (XPS) measurements were performed on a PHI Quantera SXM (ULVACPHI, Japan) employing Al mono-chromator irradiation as the photosource.

## 3. Results and discussion

The XRD pattern 1 in Fig. 1a shows two broad, distinguishable diffraction peaks, (002) and (100), corresponding to a partially graphitic structure of CBs. From the Scherrer equation [18], the crystalline graphite domain is about 1.2–3.6 nm, indicating relatively low graphitization because the primary CB particle size is about 10–20 nm. The very broad, weak peak on pattern 2 indicates a nearly amorphous structure of AC, reasonably due to the damage of the graphitic structure by chemical activation for forming AC with a highly porous structure [19]. The Raman spectra in Fig. 1b confirm the relatively low graphitization property of CBs (low G-to-D band intensity ratio,  $I_{\text{G}}/I_{\text{D}} \approx 0.98$ ) and the almost amorphous nature of ACs (very low Raman peaks).

Fig. 1c shows the N<sub>2</sub> adsorption/desorption isotherms of CB and AC particles. The hysteresis loop at high relative pressures ( $P/P_0 > 0.8$ ) on curve 1 indicates the agglomeration of CB forms a porous structure. This phenomenon suggests the excellent connection among CBs, providing 3D electron pathways and fairly good electrolyte-accessible DL capacitance although their  $S_{\text{BET}}$  is relatively low. This statement is



**Fig. 1.** (a) XRD patterns, (b) Raman spectra, and (c) N<sub>2</sub> adsorption/desorption isotherms of (1) CB and (2) AC; inset in (c) shows the corresponding pore size distributions and (d) a SEM image of CB.

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