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Improved Capacitive Energy Storage via Surface Functionalization of Activated Carbon as Cathodes for Lithium Ion Capacitors

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Abstract

Lithium ion capacitors (LICs) have the potential to combine the high energy density of lithium ion batteries and the high power density of supercapacitors into one device. In this study, we have investigated surface functionalization of activated carbon (AC) powder as the cathode for LICs with non-aqueous electrolytes. It is found that solution chemistry treatment is an effective way to impart pseudocapacitance and thus increase the specific capacitance of the AC powder. The surface functionalization has led to increases in the specific capacitance from 18 – 35 F/g to 80 – 140 F/g, while the areal specific capacitance per BET surface area has increased from 3.6 $\mu\text{F}/\text{cm}^2$ to 74.8 $\mu\text{F}/\text{cm}^2$. The latter is 3.5 times the theoretical electrical double layer value for graphene, indicating the existence of redox reactions and their great potential in enhancing the capacitance for LICs. The mechanism of capacitance improvement has been diagnosed and attributed mainly to the pseudocapacitive redox reaction on the C=O sites. In addition, the enhancement in the specific capacitance is found to vary with the composition of electrolytes, likely due to the change in wetting behavior and the size of solvated ions. This work has opened up a new route to increase the specific capacitance of low cost and widely used AC powder for LICs.

Keywords: Activated carbon; Surface functionalization; Lithium ion capacitors; Functional groups

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I. Introduction

As natural energy reserves dwindle and carbon dioxide generation increases, a global concern about energy shortages and environmental sustainability has intensified. As such, the development of renewable energy (such as solar energy, wind power, hydropower, and geothermal energy) has become a high priority for energy production. On the consumption side, vehicle electrification is of particular importance because highway vehicles alone in the U.S. consume 11.6 million barrels of oil per day. However, the development of both electric vehicles (EV) and renewable energy requires energy storage systems that have high energy and power densities simultaneously with superior cycle life and low cost [1]. Electrochemical devices such as lithium ion batteries (LIBs) have high energy densities because their storage mechanism is based on redox reactions induced by lithium ion intercalation and deintercalation into the bulk of electrode materials [2]. However, the power densities of currently available LIBs are low [2]. In contrast, supercapacitors, also called electrochemical capacitors or ultracapacitors, have high power densities because they store electrical charge in the electrical double layer (EDL) at an electrode-electrolyte interface [3,4]. However, their energy densities are low because electrical charge is stored only on the surface of the electrode [3,4] and, in most of the cases, their energy densities are often limited by available ions in the electrolyte [5–7].

In light of the limitations of LIBs and supercapacitors mentioned above, significant efforts has been devoted to developing new electrochemical storage devices that can combine the high energy density of LIBs and the high power density of supercapacitors [8,9]. Lithium ion capacitors (LICs) are a good example of these efforts [6,7,9–13]. In LICs Li sources exist in the anode in various forms such as pre-lithiated graphite or carbon, nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ attached on carbon nanofibers, and stabilized lithium metal powder (SLMP) [6,11,12]. Because of the Li source in the anode the energy densities of LICs are not limited by ion concentrations in the electrolyte and thus are much larger than those of supercapacitors [5]. In addition, LICs have larger cell voltages than supercapacitors, which also contributes to the larger energy density of LICs. The cathodes of LICs are typically made of carbonaceous materials to enhance the power densities [7,9–12]. For a supercapacitor, the energy density (E) and power density (P) are determined as follows [14]:

$$E = \frac{1}{m} \int_0^Q V(q) dq = \frac{1}{2m} C (V_1^2 - V_2^2) \quad (1)$$

$$P = \frac{dE}{dt} = \frac{1}{m(V_1 - V_2)} \int_{V_2}^{V_1} IV dV \quad (2)$$

where m is the mass of electrodes and C is the capacitance, V_1 and V_2 are the high and low cell voltage in the charge-discharge potential window ($V_1 > V_2$), respectively. The cell voltages of supercapacitors are typically limited to 2.5 – 2.7 V beyond which significant decrease in capacitance and continuous increase in internal resistance occur [9,14,15]. In contrast, due to the very negative Li-based anode, the cell voltage of LICs can be as high as 3.8 V [6,7,9,11]. As such, LICs have much larger energy density than supercapacitors because of their larger cell voltages, as mentioned before. Moreover, in full capacitors, the cell capacitance follows the following equation [16]:

$$1/C_{\text{cell}} = 1/C_+ + 1/C_- \quad (3)$$

Thus, for traditional symmetric capacitors, $C_{\text{cell}} = \frac{1}{2} C_{\text{electrode}}$ due to the series connection of two equal capacitors [17], whereas $C_{\text{cell}} \approx C_+ = C_{\text{cathode}}$ in LICs because C_{anode} is significantly larger than C_{cathode} . This leads to higher cell capacity in LICs. Other merits of LICs include low self-discharge and large operation temperature window [9,18].

The electrode materials for supercapacitors can be generally divided into two groups: (i) electrical double-layer capacitive materials such as activated carbon (AC), carbon aerogels, carbon nanotubes, carbide-derived carbons, graphene, etc. and (ii) pseudocapacitive materials that undergo pseudocapacitive redox reactions [17,19]. Pseudocapacitive materials have become more and more attractive because they hold the promise of achieving battery-level energy density combined with the cycle life and power density of supercapacitors. Conway and the research community have identified several faradaic mechanisms that can result in pseudocapacitance: (1) underpotential deposition, (2) redox pseudocapacitance, and (3) intercalation pseudocapacitance [20]. Metal oxides such as RuO_2 , MnO_2 , NiO , Fe_3O_4 , and Co_3O_4 have been studied extensively as pseudocapacitive materials [20–22], in which cations intercalate/deintercalate into the oxide surface during charge/discharge [19,23].

The cathodes for LICs can also be divided into the aforementioned two categories: EDL capacitance and pseudocapacitance. However, to the best of our knowledge, only commercial AC was reported as the cathode for LICs [7,12,24]. As such, the energy density of LICs are limited by the cathodic electrode due to its much lower capacitance than anodic electrode. Hence, the exploration of more effective cathodic electrodes is essential to improve the performance of LICs in which the non-aqueous electrolyte is indispensable. Recently, multiple

studies [25,26] have reported pseudocapacitive phenomena by creating surface functional groups on carbonaceous materials to improve the capacitance of conventional supercapacitors. For example, treatments at elevated temperature with mixtures of gases containing ammonia (Ar-NH_3 , $\text{N}_2\text{-NH}_3$, etc.) have been proposed to modify the surface functionality and porous texture of various carbons (AC powder, carbon fibers, carbonized melamine-mica composite, activated rayon char, etc.) [10,25–29]. Plasma treatment and chemical activation have also been investigated widely to impart the surface functionality and thus enhance the capacitance [30–38]. Nevertheless, most of these studies focus on surface functionalization of carbon nanotubes, carbon fibers, and graphene [31–38]. Only few studies on surface functionalization of AC have been conducted, but mainly focusing on supercapacitors with aqueous electrolytes [30,39]. To our knowledge, no studies have been devoted to surface functionalization of AC with non-aqueous electrolytes in any type of capacitors. It should be noted that AC is much cheaper and more widely used in industry than carbon nanotubes, carbon fibers, and graphene. Therefore, it is of theoretical interest and technological importance to study surface functionalization of AC and its effectiveness in enhancing the capacitance through pseudocapacitive reactions under non-aqueous electrolyte environments.

In this study, we have investigated surface functionalization of commercial AC powder through solution chemistry treatment and its effect on improving pseudocapacitance to serve as cathodes for LIC applications with non-aqueous electrolytes. It is found that even though the solution chemistry treatment leads to a decrease in the BET surface area of AC by three quarters, the capacitance has increased 3 times in both propylene carbonate (PC) and diethylene glycol dimethyl ether (Diglyme) electrolytes. Furthermore, the areal specific capacitance per BET surface area has increased from $3.6 \mu\text{F}/\text{cm}^2$ before surface functionalization to $74.8 \mu\text{F}/\text{cm}^2$ after surface functionalization. The latter is 3.5 times the theoretical EDL value for graphene, indicating the existence of redox reactions and their great potential in enhancing the capacitance for LICs. The mechanism of pseudocapacitance improvement has been diagnosed and attributed mainly to the pseudocapacitive redox reaction on the C=O sites.

II. Experimental Section

Typically, 0.3 g of activated carbon (#US1074, US Research Nanomaterials, Inc.) was added to 30 mL freshly-prepared aqueous solution of 1.0 M ammonium persulfate (APS), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Sigma-Aldrich, 99.5%), and 2.0 M H_2SO_4 (Alfa Aesar). The mixture was stirred at

60 °C for 6 h to impart surface functionalization. Then, the surface functionalized AC (f-AC) was filtered and thoroughly rinsed with deionized water, followed by drying overnight in an oven at 80 °C. This process will be termed as the H₂SO₄-APS treatment hereafter. For comparison, the obtained f-AC was annealed at 300 °C for 3 h in Ar (f-AC 300C) to achieve some degrees of thermal reduction of f-AC and to enhance our understanding of the effect of surface functionalization of AC. Commercial AC (YP-80F, Kuraray Chemical Co.) with larger specific surface area (> 2000 m²/g) was also investigated for LICs, labelled as AC_K. The same procedure was used to obtain f-AC_K.

A two-electrode coin cell configuration was used to measure the electrochemical performance of the cathodic electrodes in LICs. Electrodes were composed of 80 wt% active mass, 10 wt% carbon black and 10 wt% poly(vinylidene fluoride) binder (PVDF, (CH₂CF₂)_n, Alfa Aesar). The materials were slurry-cast from a 1-methyl-2-pyrrolidinone (NMP, alfa Aesar) suspension onto an aluminum foil. The electrodes were dried at 120 °C under vacuum for 12 h and then cut into 14.3 mm (diameter) disks. The active mass loadings are ~1.5 mg/cm². Then, the carbon electrodes were assembled into coin-type cells (CR 2032) in an argon-filled glovebox with lithium chip as the anode and polypropylene/polyethylene films (3501, Celgard, USA) as the separator. Two lithium ion containing organic electrolytes were used: (i) diethylene glycol dimethyl ether (Diglyme) solution with 1.0 M lithium trifluoromethanesulfonate (LiTFMS) and (ii) 1.0 M lithium hexafluorophosphate (LiPF₆, 99%, Alfa Aesar) with 10 vol% fluoroethylene carbonate (FEC, 99%, Sigma-Aldrich) as additives in the solution of propylene carbonate (99.7%, Sigma-Aldrich) and diethylene carbonate (DEC, 99.7%, Sigma-Aldrich) at 1:1 volume ratio. Before the battery assembling, the AC electrode was soaked in the electrolyte for 24 h.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out using a potentiostat (Parstat 4000, Princeton Applied Research). Potentialstatic EIS measurements were conducted at the open circuit voltage (OCV) with 10 mV potential amplitude under the frequency of 100 kHz to 100 mHz. CV and galvanostatic charge/discharge profiles were collected in a voltage window from 1.5 to 3.5 V vs Li/Li⁺. Galvanostatic cycles were conducted using Neware battery testing systems (CT-3008-5V1mA and CT-3008-5V10mA, Neware Technology Ltd.). The specific capacitance of cells, C_{sp} (F/g), determined from the galvanostatic cycles was calculated with the aid of the following formula [40,41]:

$$C_{sp} = \frac{I\Delta t}{m\Delta V} \quad (4)$$

where I is the charge or discharge current (A), Δt is the charge or discharge time (s), ΔV is the voltage change (V) during the charge or discharge process, and m is the mass of the active material (g) in the cathode. The typical mass loading of active material for each electrode is around 2.0 mg per cell. The specific capacity (C/g) of the investigated electrodes for LIC was also listed in Table S2 to demonstrate the stored charge per mass of the active material in each electrode.

Thermogravimetric analysis (TGA) was carried out using the METTLER TOLEDO thermogravimetric analyzer in constant air flow with ceramic pans. The data were collected with a scan rate of 2.5 to 5.0 °C/min over a temperature range of 20-850 °C. The porosity of various samples was studied via N₂ adsorption at 77 K (NOVA 2200e surface area analyzer, Quantachrome Instruments). Prior to the analysis, samples were degassed under vacuum at 150 °C for 48 h. The specific surface area was estimated using the Brunauer-Emmett-Teller (BET) equation, and the total pore volume was calculated from the amount of N₂ adsorbed at relative pressure $P/P_0 = 0.95$. The mesopore volumes were determined by the BJH model.

Transmission electron microscopy (TEM) images were recorded using an JEOL 3010 TEM. TEM sample were prepared by dispersing AC particles in isopropanol and drop-casting the suspension on carbon coated Cu grid. Infrared spectra of products were recorded on a Nicolet Nexus-IR 470 spectrometer using a KBr pellets (0.1% sample) in the 400–4000 cm⁻¹ range. Raman measurements were performed on a Renishaw inVia Confocal Raman Microscope equipped with CCD detector and 1800l/mm diffraction grating. Raman scattering was excited with 514.5 nm line of an Ar ion laser with output power less than 1mW at the powder sample. X-ray photoelectron spectroscopy (XPS) experiments were performed with a Kratos Axis-165 XPS instrument equipped with an Al source (1486.6 eV). Survey and high resolution scans were conducted using pass energy of 80 eV and 20 eV, respectively. The C1s peak of graphitic carbon at 284.6 eV was used for calibration of the energy scale. In order to eliminate adsorbed contaminants, samples were dried and degassed under vacuum at 120 °C for 24 h before the XPS measurements.

III. Results and Discussion

The morphologies of the as-received AC and surface functionalized AC have been characterized using TEM (Figure 1). The as-received AC exhibits significant agglomeration and the sizes of agglomerates range from 200 nm to 2 μm. After the H₂SO₄-APS treatment the dispersibility of f-AC in water and alcohol is improved substantially. As a result, the sizes of

agglomerates become much smaller to around 40 – 150 nm. The sizes of primary particles forming these agglomerates are found to be 20 to 40 nm (Figure 1c and 1d). Mesopores are not visible even under high magnifications of TEM, but BET analysis reveals the presence of mesopores. Table 1 summarizes the BET analysis, showing that the specific surface area (SSA) decreases from 615 m²/g to 151 m²/g after the surface functionalization treatment. Accompanied with the decrease in SSA, the volume of mesopores is also reduced significantly from 0.07 cc/g to 0.02 cc/g with the average pore diameter staying almost the same. The large reduction in both SSA and pore volume is somewhat a surprise to us. We hypothesize that these phenomena are due to the etching effect of the acid. The etching may have removed some carbon networks inside AC powder particles, leading to larger pores and thus reduced mesopores and specific surface area while maintaining the average diameter of mesopores nearly the same. The subsequent thermal treatment at 300 °C in air, however, did not cause much additional changes on specific surface area and pore size distribution (Table 1). Their pore size distribution and accumulative pore volume curves have been illustrated in Supporting Information (Figure S1). The etching function of the acid is consistent with the reduced impurities in AC after the H₂SO₄-APS treatment as described below.

Figure 1. TEM images: (a-b) the as-received AC and (c-d) the surface functionalized AC (f-AC).

It is known that active acid treatment on carbon nanomaterials can bring carboxylic, hydroxyl, epoxy, and aldehydic function groups, which in turn makes carbon materials more

hydrophilic. Here, the surface functional group change in f-AC is reflected on the change of their TGA graphs as shown in Figure 2. The weight loss Δm_1 before 150 °C increases from 3% in AC to 8.5% in f-AC, which is mainly attributed to the adsorbed moisture and gases. In addition, the weight loss between 150 °C and ~440 °C before the carbon decomposition (Δm_2) increases from almost 0% in AC to 20% in f-AC, which is attributed to the presence of defective carbon or carbon with functional groups. Therefore, the increase in Δm_2 indicates the successful surface functionalization. It should be noted that the H_2SO_4 -APS treatment also purifies AC, which can be deduced from the dramatically decreased ash content from 16.3% in AC to 3.4% in f-AC, as shown in Figure 2. The EDS analysis of AC residuals after the TGA test reveals that the ash of AC mainly contains SiO_2 , CaO , Al_2O_3 , Fe_2O_3 , etc. (Supporting Information, Figure S2).

Table 1. N_2 adsorption surface area and mesopore analysis

	SSA (m^2/g)	Pore volume (cc/g)	Average pore diameter (nm)
AC	615 ± 20	0.07	3.586 ± 0.005
f-AC	151 ± 10	0.02	3.622 ± 0.005
f-AC 300C	170 ± 10	0.02	3.614 ± 0.005

Figure 2. TGA tests of AC and f-AC under constant air flow.

The capacitive properties of AC- and f-AC-based LIC half cells are investigated using galvanostatic charge-discharge (GCD) and cyclic voltammetry (CV) measurements in the potential range of 1.5 V to 3.5 V vs Li/Li^+ . GCD tests are carried out at current densities of 12 – 60 mA/g. Figure 3 shows the GCD capacitive properties of AC, f-AC, and f-AC 300C based LICs

with the electrolyte of 1.0M LiPF_6 in PC/DEC mixed solvents (1:1) and 10 vol% of FEC additive. It is worth noting that the capacitance difference among these LIC half cells is not due to the limitation of Li ion concentrations because of the presence of the tremendous Li^+ source from the anode. As mentioned before, low Li ion concentrations in the cell can impose negative effect on the specific capacitance, especially in high surface area carbon electrodes based supercapacitors [5–7,42], but this is not the case in this study.

Figure 3. Electrochemical behaviors of AC and f-AC cells with $\text{LiPF}_6/\text{PC-DEC-FEC}$ electrolyte: (a) voltage-time plots of AC and f-AC cells during charge/discharge at different current densities, (b) galvanostatic charge/discharge curve of the AC cell, (c) galvanostatic charge/discharge curve of the f-AC cell, and (d) the specific capacitance as a function of cycle numbers.

The AC cell gives an initial specific capacitance of ~ 20 F/g and becomes stabilized at 11 F/g after 20 cycles (Figure 3). Even when the current density increases from 20 mA/g to 50 mA/g, there is almost no change in the specific capacitance, implying a very conductive electrode. It should be noted that f-AC discharge curves are more linear than that of the AC cell. At the potential close to 1.5 V the discharge curve of AC displays a near plateau instead of linear feature in the higher potential range. This non-linearity results in a slightly overestimated specific capacitance of the AC electrode based on Eq. (4) in high potential region (i.e. 2.0-3.5 V).

In spite of this overestimation for AC electrodes, the f-AC electrodes still exhibit much higher specific capacitance than AC electrodes, showing specific capacitance as high as 55 F/g which is around 3 times that of the AC electrode. Furthermore, the areal specific capacitance per BET surface area of f-AC is $36 \mu\text{F}/\text{cm}^2$ (Table 2), which is much higher than the corresponding value ($2.4 \mu\text{F}/\text{cm}^2$ only) of AC and even higher than the theoretical EDL value of graphene ($21 \mu\text{F}/\text{cm}^2$) [15,40,43]. The increased capacitance is considered to originate from the pseudocapacitive redox reactions on the functionalized AC surface since there is no plateau observed from the f-AC charge/discharge curves. This hypothesis is supported by the CV analysis (to be shown later) and consistent with the decreased specific capacitance of f-AC 300C cells which have the reduced surface functionalization because of the thermal reduction during the 300°C thermal treatment.

Table 2. The areal and gravimetric specific capacitance

Sample	Areal specific capacitance ($\mu\text{F}/\text{cm}^2$)		Specific capacitance (F/g)	
AC	2.4 ^a	3.6 ^b	8 - 16 ^a	18 - 35 ^b
f-AC	36.4 ^a	74.8 ^b	38 - 50 ^a	80 - 140 ^b

^a Capacitors with the electrolyte of 1M LiPF_6 in PC-DEC-FEC (9:9:2 V%),

^b Capacitors with the electrolyte of 1M LiTFMS in Diglyme.

The CV curves of above cells with the $\text{LiPF}_6/\text{PC-DEC-FEC}$ electrolyte have been measured to further explore the corresponding electrochemical process (Figure 4). As expected, all electrodes showed no peaks from 1.5 V/1.0 V to 3.5 V at 50 mV/s, implying the processes of charge adsorption/desorption and/or surface confined redox reactions. AC electrodes displayed quasi-rectangular shape in their CV curves, suggesting a double-layer-dominated capacitance behavior based on ionic adsorption and exchange as well as a quick charge and discharge responses. For f-AC and f-AC 300C electrodes, their CV curves show a distorted rectangular or rhombus shape but higher current density than AC which are consistent with the GCD results. Upon decreasing the scan rate from 50 mV/s to 5 mV/s and 0.5 mV/s for f-AC cells, no redox reaction peaks appear except the Li-ion intercalation into graphite carbon below 1.5 V (Figure 4b). This result is in good accordance with the nearly linear potential profiles of the GCD curves in the potential window from 1.5 V to 3.5 V (Figure 3). Thus, using Eq. (4) to approximate the specific capacitance by averaging the charges stored over the entire potential window (from 1.5 V to 3.5 V) through dividing the stored charge by ΔV (2 V in this case) is reasonable. Note that

CVs with full potential window scanning from 0.1 V to 3.5 V are illustrated in Figure S3 to show that above 1.5 V there is definitely no redox reaction peaks. The symmetry of positive and negative parts in CV curves scanned from 1.5 to 3.5 V also indicates quite good reversibility of these pseudocapacitive reactions under various scan rates in this operational potential window.

Figure 4. (a) CV curves for AC, f-AC, and f-AC 300C cells under a scan rate of 50 mV/s and (b) CV curves of f-AC cells under scan rates of 5 mV/s and 0.5 mV/s from 1.5/1.0 V to 3.5 V vs Li/Li⁺ with 1M LiPF₆ in the PC-DEC-FEC (9:9:2 V%) electrolyte.

To tackle the involved reversible redox reactions, characterization of the surface condition of these samples is needed. Hence, surface diagnostic tools such as Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and XPS have been employed. The Raman spectra (Figure 5a) exhibit two peaks at about 1350 and 1601.4 cm⁻¹, corresponding to the typical D band and G band for carbon material [44–46]. The G band at 1601 cm⁻¹ is associated with the sp² carbon atoms in the hexagonal carbon framework, while the D band at 1350 cm⁻¹ corresponds to the sp³-hybridized carbon atoms. The D and G band peaks and positions are very sensitive to the microstructure of carbon materials, including defects, disorder, edges, and carbon grain size [44–46]. Consequently, the intensity ratio of D band to G band (I_D/I_G) can be used as an indicator to evaluate the defect density in the carbon samples [47]. A slight increase of I_D/I_G ratio from 0.585 of AC to 0.630 of f-AC suggests an increase of defects and disorder due to the surface functionalization. Interestingly, the 300 °C treatment of f-AC shows the decreased intensity of D band, leading to the same I_D/I_G ratio as that of AC and indicating recovery of the material to some extent. The slight energy shift and

much lower intensity in f-AC shown in Figure 5(a) could be ascribed to chemical etching induced thinner graphite layers [48,49].

FTIR measurement has been conducted to further explore the nature of defects and surface functional groups (Figure 5b). The absorption peaks at 3600-3300, 1731, 1582, and 1300 – 1100 cm^{-1} can be ascribed to stretching vibrations of –OH, C=O in carbonyl, C-C and/or C=C, and C–O in various groups including carbonyl/carboxylic acid and epoxy C–O bonds, respectively. In the region of 1300 – 1100 cm^{-1} , two major peaks centered at 1236 and 1084 cm^{-1} are attributed to C-O stretching vibration in C-O-C and C-O-H, respectively. After the surface functionalization treatment, the C-H bending mode around 1381 cm^{-1} increases in f-AC. More importantly, the intensity of –OH (3600-3300 cm^{-1}), C=O (1731 cm^{-1}), and C-O (1236 cm^{-1}) vibration peaks increases significantly in f-AC, indicating the increased population of these functional groups in f-AC. It should be noted that the 300 °C treatment in Ar only partially eliminates these O-containing functional groups since these peaks are reduced but still stronger than those from AC.

Figure 5. (a) The Raman scattering spectra and (b) FTIR analysis of AC, f-AC and f-AC 300C as indicated. Note that the Raman intensity of f-AC is very low and has been magnified by a factor of 7 for comparison.

XPS analysis (Figure 6) shows only C and O elements in both AC and f-AC, and the oxygen content increases from 9.62 at% in AC to 20.68 at% in f-AC. The C 1s peak is composed of four Gaussian peaks with binding energies of 284.8 eV (non-oxygenated C rings, C=C/C–C), 286.3 eV (epoxy C–O–C and C–OH), 287.5 eV (carbonyl, C=O), and 288.9 eV (carboxyl, O–C=O) [28,50,51]. Closer examination of C 1s spectra revealed that the C=O and O–C=O functional groups dramatically increase in f-AC (Figure 6d), which is consistent with

FTIR results. Meanwhile, the intensities of all O-containing components are boosted in f-AC, including three peaks with binding energies at 531.8 eV, 533.4 eV, and 535.7 eV assigned to C=O, C–O, and chemisorbed O₂ (or H₂O), respectively [27,28,52–54]. There are almost no C=O peaks detected in AC from both C 1s and O 1s spectra (considering the very low O content). This is also in good accordance with the FTIR analysis. Clearly, surface functionalization only results in C-O increase by ~3%, but leads to C=O increase by 17.3% including carbonyl, aldehydic and carboxylic acid functional groups.

Figure 6. XPS spectra of AC and f-AC: (a) survey, (b) high resolution scans of C 1s, (c) high resolution scans of O 1s, and (d) the quantitative analysis of the survey and C 1s peaks.

The electrochemical behaviors of O-containing functional groups on graphene such as graphene oxide or partially oxidized graphene have been investigated both in aqueous and non-aqueous electrolyte [55–58]. However, some reports show that the redox reactions related to O-containing functional groups are not reversible so that they can't contribute to the cyclable capacitive energy storage [55–58]. Very recently, some studies have indicated that N- and O-containing functional groups on carbon nanostructures could give reversible redox reactions [27,33,59,60]. In this study both CV and GCD experiments of f-AC have revealed reversible redox reactions in the region of 1.5 - 3.5 V vs Li/Li⁺ which leads to much higher specific capacitance of f-AC than AC. The FTIR, XPS and Raman analyses indicate a dramatic increase

of C=O groups in f-AC and a decrease in f-AC 300C. The concentration evolution of C=O groups in these samples matches exactly the evolution of capacitive performance of the corresponding LICs. Therefore, we propose that the enhanced capacitance is due to the reaction of Li^+ ions with C=O functional groups as shown in Eq. (4) below,

Similar mechanism has been observed in sodium systems by K. Kang's group very recently [33,59,60].

Figure 7. (a) The voltage-time plot, (b) galvanostatic charge/discharge curves, (c) the CV at 50 mV/s of f-AC cells, and (d) specific capacitance as a function of cycle numbers of AC vs f-AC cells with the LiTFMS/Diglyme electrolyte.

Interestingly, the same trends but much higher specific capacitances have been observed in AC, f-AC, and f-AC 300C half cells with the LiTFMS/Diglyme electrolyte (Figure 7). The specific capacitances of AC and f-AC cells have increased to 35 F/g and 110 F/g, respectively, which have almost doubled in comparison with the corresponding values in the case of the $\text{LiPF}_6/\text{PC-DEC-FEC}$ electrolyte. Furthermore, the areal specific capacitance of f-AC per BET surface area has increased to as high as $74.8 \mu\text{F}/\text{cm}^2$ (Table 2), which is 2.5 times

higher than the electrical double layer capacitance of $21 \mu\text{F}/\text{cm}^2$ for graphene [15,40,43] and indicates the effectiveness of surface functionalization in enhancing the capacitance of AC materials. The significant increase in the capacitance by changing from the $\text{LiPF}_6/\text{PC-DEC-FEC}$ electrolyte to the $\text{LiTFMS}/\text{Diglyme}$ electrolyte is ascribed to the enhanced pore accessibility. A recent paper [61] has reported that Diglyme and ether based solvents give solvated ions with smaller sizes than carbonate solvents. Thus, we postulate that both good wetting and small solvated ions have improved pore accessibility, leading to the greatly enhanced capacitance in the $\text{LiTFMS}/\text{Diglyme}$ electrolyte. It is interesting to note that f-AC exhibits a larger enhancement (100% increase) in the areal specific capacitance than AC (50% increase) when the $\text{LiPF}_6/\text{PC-DEC-FEC}$ electrolyte is changed to the $\text{LiTFMS}/\text{Diglyme}$ electrolyte (Table 2). This trend is also reflected in CV scans (Figure 7c) where a very large current density ($\sim 2 \text{ A/g}$) has been obtained from the f-AC cell, whereas the correspond value of the AC cell is around 4-5 times smaller. This trend indicates that the full utilization of surface functionalized AC is more sensitive to the selection of proper electrolytes than pristine AC. Good wettability and small solvated ions are likely the major factors in these observed phenomena.

It should be mentioned that the GCD curve became more linear with the $\text{LiTFMS}/\text{Diglyme}$ electrolyte than that with the $\text{LiPF}_6/\text{PC-DEC-FEC}$ electrolyte. Considering the non-perfect linearity of GCD from the $\text{LiPF}_6/\text{PC-DEC-FEC}$ electrolyte, additional quantitative results are listed in terms of the charge stored in the electrode without averaging over the entire potential window ΔV in Supporting Information (see Table S2) [16,62,63].

Up to this point the acid treatment and electrochemical evaluation have been applied to the commercial AC with relatively low specific surface area ($615 \text{ m}^2/\text{g}$, Table 1). Furthermore, there is dramatic SSA drop and enlarged pore size after $\text{APS-H}_2\text{SO}_4$ treatment, even though ammonium persulfate (APS) based oxidants have been confirmed to be effective on maintaining the surface area and pore structure while bringing numerous O-containing groups on the surface of AC powder [64,65]. In the f-AC electrode, the capacitance is a combination from EDLC and pseudocapacitance. Thus, to further enhance the specific capacitance by utilizing the EDL and functionalized surface, another commercial AC with higher SSA ($\sim 2000 \text{ m}^2/\text{g}$ from Kuraray Chemical Co., labelled as AC_K in this study) has been investigated and chemically treated with the same procedure as f-AC. The SSA of AC_K is reduced from $2000 \text{ m}^2/\text{g}$ to $800 \text{ m}^2/\text{g}$ after the acid treatment (see f-AC_K in Table S1 and Figure S4). As expected, much larger specific capacitances have been observed in the f-AC_K half cell (Figure S5), especially for the first few cycles (200-240 F/g which are significantly higher than the specific capacitance of f-

AC). These results indicate that the specific capacitance can be enhanced by combining high SSA and surface functionalization.

Although surface functionalization can result in surface redox reactions and thus enhanced capacitance, its cycle stability is always a concern [66]. Figures 3, 7 and S5 do exhibit gradual decay in the capacitance of f-AC and f-AC_K with cycles. However, the stability of f-AC improves significantly beyond 30 cycles, particularly for the cells with the LiTFMS/Diglyme electrolyte showing little or no degradation beyond 30 cycles. Note that the significant capacitance decay before 30 cycles is also reflected in the less than 100% Coulombic efficiency (defined as the discharge capacitance divided by the charge capacitance). As shown in Figure 7, the Coulombic efficiencies are lower than 100% for both AC and f-AC at all the cycles tested, suggesting some irreversible processes in both AC and f-AC. In contrast, f-AC 300C exhibits a 100% Coulombic efficiency, indicating reversible processes for this type of AC. When the electrolyte is based on carbonates (Figure 3), the Coulombic efficiencies of all three AC electrodes are higher than 100% before 30 cycles, but become 100% after 30 cycles for both f-AC and f-AC 300C while AC without treatment still remains to have the Coulombic efficiency higher than 100% after 30 cycles. The mechanism(s) for the Coulombic efficiency higher than 100% are not clear, but these phenomena indicate that there is a transition period before stable cycles are approached.

It is noted that the LiTFMS/Diglyme electrolyte also induces faster charge/discharge processes which are reflected from the more linear curves in the voltage-time profile (Figure 3a vs 7a). However, it seems that the f-AC electrode is not conductive enough for high charge/discharge rates. When the current density is doubled from 0.017 A/g to 0.035 A/g, obvious capacitance drop occurs (Figure 7d). To understand the cause, EIS of these two-electrode LIC half cells and conductivity tests of powder materials have been conducted. Figure 8 gives typical Nyquist plots of AC and f-AC based cells. Note that the f-AC cell has a higher cell ohmic resistance, 9.7 Ω (represented by the intercept of the semicircle with the real axis) than the AC cell, 0.5 Ω . So is true for the charge-transfer resistance at the electrode/electrolyte interfaces because the f-AC cell has a larger arc than the AC cell. The higher cell ohmic resistance of the f-AC cell is likely related to the decreased conductivity of f-AC.

Figure 8. EIS Nyquist plots of AC and f-AC based half cells with the LiTFMS/Diglyme electrolyte.

Figure 9. Schematic of the cut-away of the custom-made cylindrical die set for conductivity measurement.

Thus, a custom-made setup (Figure 9) has been utilized to determine the conductivity of various AC powders. In this custom-made setup two Cu rods are employed to compress the test powder into a pellet under 300 MPa pressure. The conductivity (σ) of the sample is then determined according Eq. (6):

$$\sigma = \frac{L}{RA} \quad (6)$$

where L (cm) is the thickness of sample, A (cm²) is the cross-section area of the pellet, and R (Ω) is the resistance measured. The pristine AC is very conductive with $\sigma = 0.13$ S/cm as shown

in Table 3. Interestingly, the electrode conductivity is further increased after adding 10 wt% of non-conductive PVDF binder. We have attributed this conductivity increase to the improved contact between AC particles because of the presence of the PVDF binder which has enhanced AC particle packing. In other words, the improved powder packing has outweighed the negative effect of the high impedance of PVDF itself. As a result, the conductivity has been improved rather than decreased. The conductivity of AC, however, has been reduced to $\sim 8.5 \times 10^{-5}$ S/cm after functionalization (i.e. f-AC). In contrast, thermal treatment in an inert atmosphere can improve the conductivity as shown from f-AC 300C. However, the decrease in the redox activity is observed, likely due to lose of the C=O functional group during the thermal reduction. It is interesting to note that the electrical resistance measured in the mode of direct current (R_{DC}) is similar to that determined from the EIS mode (R_{EIS}) when the resistance is low (Table 3). However, when the resistance is high (e.g., in the case of f-AC), R_{DC} becomes significantly higher than R_{EIS} because of the polarization at the contact interface. The conductivity measurement has unambiguously revealed that surface functionalization of AC has led to a decrease in the electrical conductivity. Thus, to improve the high rate performance of functionalized AC, how to improve the conductivity while keeping the redox functionality of the f-AC electrode needs to be explored in the future. Possible methods may include a fine control in the functionalization treatment of AC or utilization of more conductive carbon materials as conductive scaffold.

Table 3. Conductivity of active materials*

Samples	l (cm)	R_{EIS} (Ω)	σ_{EIS} (S/cm)	R_{DC} (Ω)	σ_{DC} (S/cm)
AC	0.053	0.472	0.130	0.506	0.122
AC-PVDF(10 wt%)	0.085	0.549	0.180	0.576	0.171
f-AC	0.052	707.7	8.53E-5	2160	2.80E-5
f-AC 300C	0.059			16.4	4.18E-3

* l , R , and σ are defined in Eq. (5). The subscripts EIS and DC stand for the mode of measurements using electrochemical impedance spectroscopy and direct current, respectively.

Conclusion

In this study, we have investigated surface functionalization of commercial AC powders through solution chemistry treatment and its effect on improving pseudocapacitance to profit from the low cost AC material, high cell voltage and large stable window, thereby a high energy

and high power density cathode for LICs with non-aqueous electrolytes. It is found that via simple chemical surface functionalization the specific capacitance of AC is increased 3 times although the specific surface area is reduced by three quarters. The FTIR, XPS and Raman studies reveal dramatic increase of C=O groups in f-AC and a decrease of that in f-AC 300C. The concentration evolution of C=O groups in these samples matches exactly the evolution of capacitive performance of the corresponding AC cells. Therefore, it's believed that Li⁺ reversibly reacts with C=O functional groups between 1.5V – 3.5 V vs Li/Li⁺. This gives pseudocapitance and is the major mechanism for the increased specific capacitance. The pseudocapacitive reactions also enhance the areal specific capacitance from 3.6 $\mu\text{F}/\text{cm}^2$ to 74.8 $\mu\text{F}/\text{cm}^2$, significantly higher than the theoretical EDL value of graphene. In addition, the exploration of two different organic electrolytes reveals that the LiTFMS/Diglyme electrolyte is far more efficient in enhancing pseudocapitance than the carbonate electrolytes. This trend has been attributed to the improved wetting and smaller solvated ions provided by the LiTFMS/Diglyme electrolyte. This work has opened up a new route to increase the specific capacitance of low cost and widely used AC powder for Li-ion capacitors.

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