Effect of salt concentration in water-in-salt electrolyte on supercapacitor applications

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ABSTRACT

Electrical double-layer supercapacitors offer numerous advantages in the context of energy storage; however, their widespread use is hindered by the high unit energy cost and low specific energy. Recently, water-in-salt (WIS) electrolytes have garnered interest for use in energy storage devices. Nevertheless, their direct application in high-power devices is limited due to their high viscosity. In this study, we investigate the WIS Lithium bis(trifluoromethanesulfonyl)Imide (LiTFSI) electrolyte, revealing a high specific capacitance despite its elevated viscosity and restricted ionic conductivity. Our approach involves nuclear magnetic resonance (NMR) analysis alongside electrochemical analyses, highlighting the pronounced advantage of the WIS LiTFSI electrolyte over the WIS LiCl electrolyte at the molecular level. The NMR analysis shows that the LiTFSI electrolyte ions preferentially reside within the activated carbon pore network in the absence of an applied potential, in contrast to LiCl where the ions are more evenly distributed between the in-pore and ex-pore environments. This difference may contribute to the difference in capacitance between the two electrolytes observed during electrochemical cycling.

Keywords

Supercapacitor, Water-in-salt electrolyte, LiTFSI, LiCl, NMR

**1. Introduction**

A detailed understanding of electrolyte properties is crucial for ongoing advances in the field of electrochemical energy storage, particularly for batteries and supercapacitors (SCs). In recent decades, there has been a tremendous effort to discover more efficient electrolytes [1-5]. The current state-of-the-art for SCs involves the use of organic electrolyte, such as acetonitrile [6] or propylene carbonate [7], with optimized salt content typically based on tetralkylammonium cations. While these electrolytes offer good ionic conductivity and a wide electrochemical stability window (ESW), they may exhibit degraded device performance, especially over extended cycles [6-10]. Significant research has also been conducted on ionic liquids, known for their wide operational ESW. However, their high viscosities reduce their ionic conductivity, and their elevated cost and complex purification processes limit their applicability [11]. On the other hand, more environmentally friendly aqueous electrolytes with high ionic conductivity and low cost, show great potential in the field of SCs [3, 12-14]. However, the operational voltage range of these devices is constrained by water decomposition, restricting them to a narrow ESW (thermodynamically < 1.23 V). This limitation poses a significant challenge in achieving high energy density outputs for application in SCs [12-14]. To enhance the electrochemical stability of aqueous electrolytes, various organic additives, including ethylene glycol (EG) [15], poly(ethylene glycol) (PEG) [16], and dimethyl sulfoxide (DMSO) [17], have been utilized. The introduction of these organic additives alters the solvation structure of cations by forming strong hydrogen-bonding interactions with water. This modification disrupts the original hydrogen-bond network of water, leading to a reduced activity of water in the electrolyte.

A parallel development in the battery field has been the application of highly concentrated water-in-salts (WIS) phases, allowing for an expansion of the operating ESW to values normally achieved only with non-aqueous electrolytes (> 3 V) [18-21]. The broad operating ESW of SCs can be attributed to their reliance on ion adsorption and desorption processes at the electrode surfaces, rather than chemical reactions. Under conditions of extremely high salinity, the electrolyte, including water molecules coordinated with salt ions, remain stable, enabling a wide range of operating voltages.[22-27]. In the initial WIS work on Lithium bis(trifluoromethanesulfonyl)Imide (LiTFSI) electrolytes in the battery context, the ESW was extended to ~ 3 V with a 21 m salt concentration [18]. The maximum ESW of this result can be attributed to the interaction between water molecules and anions [21,24], resulting in a varying ESW depending on the WIS-type electrolytes, e.g. 2.7 V for 17 m NaClO4 [28], 2.1 V for 12 m NaNO3 [29] (using activated carbon with 3-electrode configuration), and 2.5 V for 32 m KCH3COO + 8 m LiCH3COO (using Highly ordered pyrolytic graphite with 3-electrode configuration) [30]. However, the fundamental properties governing the electrosorption mechanism at the molecular/ionic level are not well understood, largely because of a lack of microscopic probes able to study the electrolyte/electrode interactions.

In particular, nanoporous activated carbon, primarily employed as an electrode for SCs, exhibits high performance owing to its significant specific surface area and excellent electrical conductivity [31,32]. However, it also demonstrates intricate ion transport properties that depend on the pore structures [33]. To comprehend this complexity, various analytic techniques are employed, such as the electrochemical quartz microbalance [34], small-angle X-ray and neutron scattering [35,36], as well as spectroscopic methods like Raman/FTIR [37] and solid-state nuclear magnetic resonance (NMR) [38-40]. Notably, solid-state NMR has recently emerged as a suitable technique for elucidating electrolyte adsorption, pore properties of carbon electrodes, and understanding the charging/discharging mechanisms of SCs through in-situ analysis [38-40]. Importantly, this technique has revealed that the pores of carbon electrodes contain abundant electrolyte ions prior to polarization, and the charging mechanism may involve ion exchange with ion adsorption, along with simultaneous counter-ion adsorption and co-ion desorption from the electrode surface [38].

In this study, we investigate the SC behavior of the LiTFSI electrolyte in a WIS system, examining its performance across varying concentrations. The key to the observed stability lies in the high salt concentration, which leads to the formation of an interfacial electrolyte layer. This layer plays a crucial role in suppressing side reactions, particularly water splitting, thereby enhancing the overall stability during electrochemical processes. To underscore the advantages of the TFSI anion, we compare the LiTFSI WIS electrolyte with the WIS phase of LiCl. This comparative analysis serves to highlight the distinctive benefits offered by the TFSI anion in the electrolyte system. In pursuit of molecular-level insights, we employ NMR analysis to study the uptake of ions by the electrodes. The comparison between WIS LiTFSI and LiCl electrolytes through NMR reveals striking differences in the in-pore ion population. This granular understanding at the molecular level provides a solid foundation for elucidating and rationalizing the observed variations in electrochemical reactions. Therefore, this study not only explores the SC behavior of LiTFSI electrolyte in a WIS configuration but also unveils the critical role of high salt concentration in stabilizing the system.

2. Experimental

2.1. Electrode preparation

YEC-8a activated carbon (Fuzhou Yihuan Carbon, China), C750 graphene nano-platelets (XGSciences, USA, now discontinued) and Polytetrafluoroethylene (PTFE, 60 wt % dispersion, Sigma-Aldrich, UK) in a 8:1:1 mass ratio were dispersed in *iso-*propyl alcohol (IPA, Fisher Chemical, UK). The slurry was stirred for at least 2 hours until most of the solvent had evaporated to achieve a non-sticky, mouldable consistency. The flattened film was rolled into 50 µm sheets using an Electric Cold Roller Press (model MSK-HRP-MR100DC MTI, KJ Group, USA). The sheets were dried in an oven at 70 °C for one hour, then transferred to a vacuum oven and dried overnight at 100 °C. Dried sheets were punched into discs of 12 mm diameter (approximately 7.8 mg).

2.2. Physical characterization

The surface morphologies were confirmed by scanning electron microscopy (SEM) performed on FEI Quanta 650 FEG ESEM at 20 kV. The specific surface area of the materials was calculated using the Brunauer-Emmett-Teller (BET) isotherm and two-dimensional non-local density functional theory (2D-NLDFT) methods [41], to find the average pore size and distributions. The chemical compositions of elements were characterized by hard X-ray photoelectron spectroscopy (HAXPES). HAXPES was performed using monochromated Ga Kα X-ray radiation (9250 eV, 3.57 mA emission at 250 W, micro-focussed to 50 m) and an EW-4000 high voltage electron energy analyser (HAXPES-Lab, Scienta Omicron GmbH); the instrument has a base vacuum pressure of ∼5 × 10−10 mbar. The HAXPES instrument also has a monochromated Al Kα X-ray source (1486 eV, 20 mA emission at 300 W) for surface sensitive XPS at the same sample position. Charge neutralisation for insulating samples is achieved using a low energy electron flood source as required (FS40A, PreVac). Binding energy scale calibration was performed using the C 1s photoelectron peak at 284.8 eV.

Viscosity was measured using an Ubbelohde viscometer, and ionic conductivity values were obtained with a conductivity meter (Seven Excellence with an Inlab 731 4-pole cell and pH electrode InLab Excert Pro-ISM, Mettler Toledo, Switzerland) at a temperature of 25 °C.

2.3. Electrochemical characterization

All the electrochemical investigations were performed in Poly(etheretherketone) (PEEK) Swagelok-type cells by sandwiching a porous glass microfiber membrane (Whatman, thickness = 0.20 mm) between two electrodes and graphite foil current collectors. For the electrolyte stability investigations, three-electrode cells were built with a working AC electrode (~7.8 mg), a greater mass of AC (~30 mg) as a counter electrode and a silver-wire pseudo-reference electrode. All the cells were filled with the 1, 5 and 20 mol·kg−1 (m) LiTFSI or LiCl electrolyte solutions. The electrochemical measurements in three-electrode cells were conducted by cyclic voltammetry (CV) at 1, 10, and 100 mV·s−1 and the galvanostatic charge and discharge method at 1, 2, 5, 10 A·g−1 with the working electrode swept between 0-0.5 V (positively) and −0.5-0 V (negatively) polarized vs the Ag wire quasi-reference electrode (AgQRE), respectively. The AgQRE (−0.161 V vs. Ag/AgCl in 3 M KCl) was calibrated using a 10 mM ferrocene solution in the room-temperature ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM TFSI).

2.4. Nuclear magnetic resonance

NMR measurements were performed using a 400 MHz Bruker Avance III HD WB spectrometer operating at a magnetic field strength of 9.4 T. YEC-8a powder (13 mg) was packed into 3.2 mm outer-diameter zirconia rotors and electrolyte solutions (22.5 µL) were injected with a microsyringe. The magic-angle spinning (MAS) rate was 5 kHz. For each sample the recycle interval was set to at least 5 × T1 (as measured by a saturation recovery experiment) and the 90° pulse length was optimized for each sample to ensure that spectra were recorded under quantitative conditions. All NMR spectra were deconvoluted using the DMfit program [42] to yield integrated resonance intensities with a Gaussian-to-Lorentzian ratio between 0 and 1. All spectra were well fitted with a single peak for the in-pore resonance and a single peak for the ex-pore resonance.

3. Results and Discussion

Fig. 1a displays the SEM image of an as-prepared activated carbon electrode (YEC-8a/C750/PTFE, 8:1:1 wt.%). The nanoporous activated carbon particles exhibit an irregular shape with a relatively coarse morphology, ranging in size from 2 µm to 20 µm. The activated carbons also contain a mixture of C750 (as a thermal conductivity enhancer) and PTFE (as a binder). The surface area and pore size of the electrode were determined through measurement of the N2 adsorption/desorption isotherm. According to the IUPAC classification of isotherm types, the activated carbon exhibits a Type I isotherm (Fig. 1b), with a calculated surface area of 1526.0 m2 g−1. Fig. 1c illustrates the pore size distribution of the activated carbon, determined using the 2d-NLDFT method [41], showing a maximum peak at 6 Å pore size and a pore volume of 1.039 cm3 g−1. The chemical composition of activated carbon was analyzed by HAXPES. As expected, the main peak in the C 1s spectrum (Fig. 1d) indicates a binding energy of 284 eV, indicative of graphitic carbon. Additionally, contributions from C=O and C-O bonds are observed. The O 1s spectra in Fig. 1e reveals a surface oxygen peak at 532 eV, corresponding to the presence of carboxyl groups, in addition to surface oxygen groups. These groups, related to the activation of carbon, are polar in nature [43]. The F 1s spectra (Fig. 1f) of the prepared electrode exhibit a peak at the binding energy of 688 eV, corresponding to fluorine in the PTFE binder [44].

The viscosity of both electrolytes increases continuously with salt concentration (Fig. S1a). On the other hand, the ionic conductivity demonstrates an increase with higher salt concentration until reaching a maximum value (around 5 m), followed by a decrease to saturation with higher salt concentrations (Fig. S1b), these findings are consistent with previous literature [45]. Ionic conductivity is influenced by both viscosity and the degree of dissociation, i.e. number of charge carriers [46]. In dilute solution, i.e. salt concentrations below 5 m, both charge carrier and viscosity increase as more ions are dissolved. However, the increase in charge carriers is more dominant, resulting in an overall improvement in ionic conductivity. In highly concentrated solutions, the increased presence of ion pairs and ion clusters, coupled with a limited number of free solvent molecules, contributes to a notable reduction in the degree of salt dissociation. As a consequence, the rising viscosity further impedes the mobility of ions, resulting in overall ionic conductivity. That is, the high concentrations of water-in-salt (WIS) electrolyte system follow the hopping process through a cooperative mechanism, similar to that of non-aqueous electrolyte systems [47].

To verify the electrochemical performance of the different concentration of LiTFSI and LiCl electrolytes, cyclic voltammograms (CVs) were recorded on separate electrodes under positively and negatively polarization at a scan rate of 1 mV·s−1, as shown in Fig. 2a,d (scan rates of 100 mV·s−1 and 10 mV·s−1 are displayed in Fig. S2 and Fig. S3, respectively). In Fig. 2a, 20 m of LiTFSI WIS electrolyte exhibits the highest specific capacitance, while 1 m has the lowest specific capacitance (the values are presented in Table S1). At higher scan rates, the CVs do not maintain a symmetric, “rectangular” shape. However, for LiCl, the capacitive response is evident at both high and low scan rates. This indicates that the small hydrated Cl- (hydrated radius ~ 0.32 nm [48]) has unobstructed accessibility to the carbon pores, and conversely, the larger TFSI ions (hydrated radius 0.8 nm [49]) can be forced into the pores of the carbon mainly at slow scan rates.

The CV results of LiTFSI for the 5 m and 20 m concentrations show similar capacitance values for the slow scan rate. This trend in capacitance values is also evident in the constant current curves obtained at relatively small current densities shown in the galvanostatic charging/discharging profile (in Fig. 2b,c and Fig. S4). On the other hand, the electrochemical behavior of both 1 m LiTFSI and 1 m LiCl not only exhibits the smallest capacitance value but also demonstrates different properties from those of 5 m and 20 m solutions, especially at the negatively polarized electrode. This is because at more dilute concentrations, i.e. 1 m, the high density of water molecules in the system decreases overpotential for hydrogen evolution, resulting in the appearance of a negative current representing the electrochemical reduction of water by chemisorption on the porous carbon electrode [50,51]. At this point, it is crucial to note that during the reduction of water to produce hydrogen, the hydroxide anions (OH-) generated alongside hydrogen ions may become partially sequestered within the porous carbon electrode. This phenomenon results in a localized increase in pH proximal to the electrode, leading to an elevated concentration of hydroxide ions and, consequently, a negative shift in the Nernst potential within that specific region [52]. This is also observable with 5 m of LiTFSI at the negatively polarized electrode (Fig. 2d,e and Fig. S5), where the discharge slope is slightly changes at –0.4 V, marking the beginning of the Faradaic reaction. In addition, the 20 m LiCl shows more resistive polarization of CV curves in Fig. 2d, indicating slow ion migration at the carbon electrode due to its poor ionic conductivity. The specific capacitance values in Table 1, are calculated from galvanostatic charge/discharge curves (for the negatively polarized electrode, calculated from 0 to –0. 35 V). The values are closer to those reported in literature values than those derived from CV (see Table S1), although they also show higher values at the negatively polarized electrode. The situation becomes clearer when we calculate coulombic efficiency from galvanostatic charge and discharge curves (η = time for discharging / time for charging × 100) shown in Table S2. For the positively polarized electrode, all the values indicate ideal capacitance behavior. However, at the negatively polarized electrode, the values exceed 100 (except for 20 m) for both electrolytes, suggesting an undesired reaction during the discharge process.

Electrochemical impedance spectroscopy (EIS) measurements were performed on SCs using both WIS electrolytes with the above concentrations. Nanoporous activated carbon electrodes immersed in electrolyte on SCs can be described as a series connection of the electrolyte resistance (*Re*) and the impedance of the porous carbon electrode [53]. As is well known, the slow scan rate of CV method usually represents a quasi-equilibrium state of a charged SC electrode [54], whereas the EIS results reflect various rapid kinetics steps, as well as quasi-equilibrium conditions evaluated at low frequencies. At low frequencies from the Nyquist plot in Fig. S6a (LiTFSI) and Fig. S6c (LiCl), the plot shows a capacitive straight line nearly perpendicular to the real axis (phase angle: 20 m ≈ 5 m > 1 m). At intermediate frequencies, disturbances affecting the migration of ions inside the pore shift the capacitive straight line to more resistive values along the real axis [55]. At high frequencies, in general, the intersection of the plot with the real axis is represented by *Re*, and the system displays resistor-like behavior. However, internal resistance, including electrode resistance and electrolyte resistance, is more complicated, especially in WIS system with nanopores. Therefore, we calculate the capacitance of *C*(*ω*), a complex form of another approach to analyze the impedance response of SCs (see Supporting Information), defined as *C'(ω)* and *C*''(*ω*) for the real and imaginary parts, respectively. The real and imaginary parts of the capacitance are expressed as a function of frequency.

 Fig. 3a,c show part of the actual capacitance as a function of frequency for electrolyte concentrations of LiTFSI and LiCl. Notice that the *C'(ω)* of the capacitance increases rapidly with decreasing frequency, which eventually becomes less dependent on frequency. This confirms that the concentration of 20 m gives the highest capacitance for both electrolytes, a behavior similar to that observed in CV and GCD studies in Fig. 2, confirming internal consistency between different experimental approaches. The *C''(ω)* exhibits a maximum at the frequency *f*0, where the relaxation time constant is defined as *τ*0 = 1/*f*0, and this behavior is characteristic of electrical double layer capacitances (EDLCs) for ion transport through the electrode microstructure [55,56]. In order words, a reduced *τ*0 value defines a faster rate of ions transported from the electrode. The relaxation time constant (*τ*) determined using the EIS techniques, which correlates with the electrolyte concentration, shows different behavior from the ionic conductivity [53]. As shown in Fig. 3b,d, the values of *τ*0 confirm that for both LiTFSI and LiCl, the electrolyte concentration at 5 m (LiTFSI = 38.02 s, LiCl = 38.02 s) has a higher value than at 20 m (LiTFSI = 19.95 s, LiCl = 10.47 s), where the charge transfer process requires a longer time scale. Comparisons of 1 m concentrations [57] involving electrochemical side-reactions that can further increase the time constant are not relevant here. In general, the understanding of EDL structures in the presence of highly concentrated WIS systems is very complex. To investigate this further, we performed NMR analysis.

Fig. 4a shows 7Li MAS NMR spectra of 13 mg of YEC-8a powder soaked with 22.5 µL of each electrolyte at different concentrations. In each spectrum, two distinct resonances are observed. Peaks at higher (more positive) chemical shift values correspond to 7Li in excess electrolyte outside of the carbon particles (ex-pore) and appear at chemical shifts very close to those of the neat solutions (Fig. S8). Peaks at lower chemical shifts (more negative) correspond to 7Li in electrolyte within the carbon pores (in-pore). The origin of the shift difference between in-pore and ex-pore environments is the magnetic field-induced ring currents associated with the delocalized electrons within the carbon surface [58,59]. These ring currents induce a secondary magnetic field which shield nuclei in close proximity (within a few Å) from the main magnetic field. Since the ring current shielding effect is strongly distance dependent [60], only species adsorbed within the micropores are shifted, and species within the excess electrolyte outside the carbon particles remain at a chemical shift close to that of the bulk electrolyte.

For LiCl, in-pore and ex-pore resonances are observed for all concentrations, showing that the Li+ species are distributed between both environments at the electrolyte loading level used. Since the NMR spectra are quantitative, the ex-pore (bulk) and in-pore contributions can be determined by integration of the corresponding resonances. The integrated intensity of the in-pore resonance grows with concentration, showing that increasing the concentration of the electrolyte results in a higher in-pore ion population. For LiTFSI, the spectrum for the 1 m electrolyte shows only an in-pore resonance: this shows that Li+ species are preferentially adsorbed from the electrolyte into the in-pore environment. For 5 m and 20 m, both in-pore and ex-pore resonances are observed showing that at these concentrations, Li+ is distributed between the two environments.

Fig. 4b shows 1H MAS NMR spectra of the same samples. In all spectra, two environments are observed, showing that the H2O is distributed between the in-pore and ex-pore environments in all systems studied. There is a noticeable reduction in the chemical shifts for the 20 m sample; this is attributed to a concentration dependence of the 1H chemical shift, whereby the chemical environment of H2O in this system (water-in-salt) is markedly different to the other electrolytes (concentrated salt-in-water).

By deconvoluting the 7Li and 1H resonance intensities, it is possible to quantify the species in each environment, and to determine a local concentration, or rather the Li+/H2O molar ratio (Figs. 4c,d and Fig. S7). For LiCl, it can be seen that for all bulk electrolyte concentrations the in-pore and ex-pore molar ratios are quite close to that of the bulk electrolyte, showing that Li+ and H2O are approximately equally distributed between the in-pore and ex-pore environments. At 20 m, the in-pore molar ratio is slightly lower than the bulk molar ratio, suggesting that there is a slight preference for ions to reside outside the pores at this concentration. In contrast, for LiTFSI, the in-pore molar ratio is higher than the ex-pore molar ratio for each electrolyte concentration. This shows that there is a clear preference for Li+ to reside inside the micropores rather than the ex-pore electrolyte, and as such the system exhibits strongly “ionophilic” character in the terminology introduced by Kondrat & Kornyshev [61]. Differences in the in-pore ion occupancies have previously been observed for more dilute aqueous electrolytes and were rationalized in terms of specific ion effects stemming from differences in hydration strength and energetic barriers for partial desolvation upon pore entry [62]. Although the cations studied here (Li+) are the same in each case, it has been previously shown that specific anion effects can also have a marked influence on the distribution of the cations between the in-pore and ex-pore environments [63], where less strongly hydrated anions tend to lead to higher in-pore electrolyte concentration. Given the relatively small pore size of the YEC-8a carbon used here (peak value of 6 Å), it is feasible that the distribution of ion populations in the lower concentration (1 & 5 m) electrolytes could be influenced by the propensity of ions to (partially) desolvate in order to enter the pores. Although the TFSI– anion is larger than Cl– (hydrated radius), it has a relatively low charge density meaning it should be less strongly hydrated, which is in line with the observation of the more ionophilic character of the system containing this electrolyte. For the high 20 m electrolyte, it is not so obvious that hydration strength should be a dominant factor since each ion is only associated with 2.78 H2O molecules on average. However, ion-ion and ion-surface interactions may also come into play, whereby the lower charge density of the TFSI– anion may still facilitate local rearrangement of the liquid structure in order for ions to enter the pores.

The differences in pore wetting between the two electrolytes may offer some insight into the measured capacitance differences, although it is difficult to draw direct links since the NMR measurements were carried out in the absence of an applied potential. For the 1 m electrolytes, the NMR-derived in-pore molar ratios are quite similar, and in this case the higher positively polarized electrode capacitance of the LiCl electrolyte may reflect its lower viscosity and higher conductivity. For the 5 m and 20 m electrolytes, the in-pore molar ratio of LiTFSI is higher and the positively polarized electrode capacitance of LiTFSI is also higher. This could suggest that a higher in-pore ion concentration can lead to higher capacitance although a wider range of electrolytes and concentrations would be require study to confirm this. We note that the relative magnitudes of the capacitances of the negatively polarized electrodes show the opposite behavior, although there is greater uncertainty in the values for LiCl here owing to the distortions observed in the electrochemical data.

**4. Conclusions**

In conclusion, we have confirmed the characteristics of two types of WIS electrolytes, LiTFSI and LiCl, as SCs through a range of electrochemical analyses. WIS LiCl shows a decrease in capacitance as the concentration increases, which we attribute to its high viscosity and low ionic conductivity, whereas LiTFSI has similar or higher capacitance values at high concentrations, despite its higher viscosity. Further insight is provided by NMR spectroscopy, which reveals ion populations in the in-pore and ex-pore environments of the activated carbon electrode. In particular, it has been observed from 7Li and 1H NMR that for LiTFSI electrolytes, Li+ cations reside preferentially within the pores of YEC-8a activated carbon in the absence of an applied potential. This is attributed to the weaker hydration strength of the TFSI anion, which facilitates the rearrangement of electrolyte species necessary for pore entry. In contrast, the LiCl - YEC-8a system shows less “ionophilic” behavior, with Li+ ions distributed more evenly between the in-pore and ex-pore environments. The specific anion effects observed by NMR may help to explain the differences in electrochemical properties of the two electrolytes studied, whereby the greater propensity for LiTFSI to access the electrode pore structure could contribute to the capacitance being maintained at high concentrations.

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**Figure Captions**

**Figure 1.** (a) Scanning electron microscopy (SEM) image, (b) N2 adsoprtion-desoprtion isotherms, and (c) size distribution of free-standing YEC-8a/C750/PTFE electrode; XPS high resolution peak of free-standing electrode for (d) C 1s, (e) O 1s, (g) F 1s.

**Figure 2.** Electrochemical performance of free-standing electrode using a three-electrode configuration. (a) CVs at scan rate of 1 mV·s−1, and galvanostatic charge-discharge curves at the (b) positively and (c) negatively polarized electrodes, respectively, with current density of 1 A·g−1 in 1, 5, 20 m LiTFSI electrolytes; (d) CVs at scan rate of 1 mV·s−1, and galvanostatic charge-discharge curves at the (e) positively and (f) negatively polarized electrodes, respectively, with current density of 1 A·g−1 in 1, 5, 20 m LiCl electrolytes.

**Figure 3.** (a) Real and (b) imaginary part of capacitance of 1, 5, 20 m LiTFSI electrolytes; (c) real and (d) imaginary part of capacitance of 1, 5, 20 m LiCl electrolytes and (f) complex capacitor.

**Figure 4.** (a) 7Li and (b) 1H MAS NMR spectra of LiTFSI and LiCl electrolytes adsorbed on YEC-8a. Li+/H2O molar ratios for the in-pore and ex-pore environments at different bulk concentrations are shown for (c) LiTFSI and (d) LiCl.

Figure 1



Figure 2



Figure 3



Figure 4



Table 1: Calculated specific capacitance (quoted as F g−1) from cyclic voltammetry results for the various electrolytes studied. Values are estimated to be accurate to a relative error of ±5%.

|  |  |  |  |
| --- | --- | --- | --- |
|  | **20 m** | **5 m** | **1 m** |
| **LiTFSI** | **LiCl** | **LiTFSI** | **LiCl** | **LiTFSI** | **LiCl** |
| positive electrode | 138 | 113 | 145 | 104 | 86 | 96 |
| Negative electrode | 159 | 144 | 212 | 197 | 146 | 90 |