Silica-grafted ionic liquids for revealing the respective charging behaviors of cations and anions in supercapacitors

Qingyun Dou1,2, Lingyang Liu1,2, Bingjun Yang1, Junwei Lang1 & Xingbin Yan1

Supercapacitors based on activated carbon electrodes and ionic liquids as electrolytes are capable of storing charge through the electrosorption of ions on porous carbons and represent important energy storage devices with high power delivery/uptake. Various computational and instrumental methods have been developed to understand the ion storage behavior, however, techniques that can probe various cations and anions of ionic liquids separately remain lacking. Here, we report an approach to monitoring cations and anions independently by using silica nanoparticle-grafted ionic liquids, in which ions attaching to silica nanoparticle cannot access activated carbon pores upon charging, whereas free counter-ions can. Aided by this strategy, conventional electrochemical characterizations allow the direct measurement of the respective capacitance contributions and acting potential windows of different ions. Moreover, coupled with electrochemical quartz crystal microbalance, this method can provide unprecedented insight into the underlying electrochemistry.
Electrochemical double-layer capacitors (EDLCs, also called supercapacitors) based on porous activated carbons (ACs) are promising energy storage devices owing to their high power density, fast charge/discharge capability, and ultra-long cycle life.1-12. In EDLCs, electrolytes, like AC electrodes, are useful in directly determining the overall performance of the devices.13-18. The calculation formula of energy density ($E = \frac{1}{2} CV^2$), where $E$ is the energy density, $C$ is the specific capacitance, and $V$ is the operating potential window indicates that the $E$ of the device greatly depends on the $V$ of electrolytes. Ionic liquids (ILs) have wider operating potential windows, lower vapor pressures, and better chemical and thermal stability than aqueous electrolytes and are thus frequently used as non-aqueous electrolytes.19-24. Furthermore, ILs exhibit remarkably increased energy densities and wide applicable temperature ranges; thus, they are considered promising electrolytes for EDLCs.8, 25, 26, 27, 28.

ILs are composed of organic cations and organic or inorganic anions, and numerous cations and anions can be selected for IL combinations.10, 16, 17. These cations and anions have distinctly asymmetrical chemical structures, and thus the positive and negative electrodes of EDLCs in IL electrolytes exhibit unequal working potential distributions and variable electrochemical behaviors14, 18-21. Furthermore, the charge storage capacities of ACs in EDLCs can be directly affected by the types and molecular structures of cations and anions of ILs.3, 4, 19, 20. Therefore, studying the effects of the intrinsic structures of cations and anions on the capacitive properties of ACs and determining the real charge storage mechanisms of EDLCs in IL electrolytes are necessary for the proper selection of ILs and rational design of high-performance EDLCs.22, 23.

Many computational simulations and instrumental analysis methods have been developed for the characterization of the storage mechanisms of ACs of EDLCs in ILs. The charge storage behaviors of AC electrodes in ILs can be understood from the theoretical level through computational simulations; the capacitance and ion dynamics of EDLCs strongly depend on factors, such as relative pore or ion size, confinement effect,26-28 and ionophilic/ionophobic pores.29-30. Simulations must undergo necessary simplifications such that simulation time and accuracy are effectively balanced. Consequently, they usually do not include all details of complex porous and electronic structures of ACs at experimental conditions. By contrast, reported instrumental analysis methods using infrared (IR) spectroscopy31, 32, small-angle neutron scattering (SANS)33-35, electrochemical quartz crystal microbalance (EQCM)36-44, and nuclear magnetic resonance (NMR)44, 45-50 are effective techniques and can be effectively used for the observation of variations in ion concentration in AC pores during charging or discharging; additionally, purely perm-selective behaviors (adsorption of counter-ions, which have an electric charge opposite to that of electrodes) and ion swapping behaviors (adsorption of counter-ions, together with the desorption of cations, which have the same electric charge as that of electrodes) occur during the polarization of AC electrodes.22, 23, 24. Cations or anions of an IL can be individually monitored through an IR technique because each type of ions has its own characteristic signal in the IR spectrum. Meanwhile, SANS can be used for the direct characterization of ions in differently sized pores, and the dynamic capability of EQCM allows real-time measuring of changes in electrode mass during charging. NMR is an effective detection technique with excellent elemental selectivity. The peak area in an NMR spectrum is proportional to the corresponding ion concentration. Moreover, NMR can be used for the selectively monitoring of in-pore ions with resonances shifting to a frequency lower than that of ex-pore ions. Therefore, in-pore cations and anions can be separately characterized and their concentrations can be fully quantified through NMR. Nevertheless, IR, SANS, EQCM, and NMR require specialized and expensive instruments, and have their respective analytical limitations.22. Thus, for the in-depth understanding of the energy storage mechanisms of EDLCs, universal experimental methods that can characterize the influences of various cations and anions of ILs on the charge storage of ACs need to be developed.

EDLCs use porous ACs with high specific surface area and uniform pore size distribution. When only one type of ion (either cation or anion) of an IL is allowed to enter carbon pores, the respective electrochemical behaviors of cations and anions in carbon pores can be analyzed. To this end, we develop an organic synthesis strategy for silica nanoparticle-grafted ILs to realize this idea (Fig. 1). In these synthetic SiO2-grafted ILs, only one ion is free, and the ion used for balancing the charge is directly attached to silica nanoparticles. Moreover, ACs are selected as study samples. Their pore sizes are less than the diameter of silica nanoparticles. We find that, when the SiO2-grafted ILs are used as electrolytes for AC electrodes, the ions covalently attached to silica nanoparticles are restricted to access to the AC pores, and only the free ion is able to enter the pores during charging or discharging (Fig. 1d). Thus, free ions in pores can be quantitatively analyzed through conventional electrochemical tests. By using AC electrodes, we are able to directly measure the capacitance contributed by cations and anions, and we find that each ion is adsorbed or desorbed within its own specific potential window during charge storage. Combination of the measurement results of respective charging behaviors of cations and anions with the results of EQCM investigation implies that purely perm-selective behavior, which is determined by the nature of ions, is dominant at a high polarized window, and only counter-ion adsorption contributes capacitance; by contrast, perm selectivity and ion swapping both occur at a low polarized window, which is determined by the competition between counter-ions and co-ions.

Results

Material synthesis and characterization. Four types of SiO2-grafted ILs were synthesized through the aforementioned organic synthesis methods. Methyl imidazolium cation (MIM+)31, 52 and trifluoromethanesulfonyl imide anion (NTf2−) were covalently attached to 7 nm commercial silica nanoparticles (LUDOX SM-30 colloidal silica, Aldrich). Meanwhile, MIM+ or NTf2− possesses an ionic moiety that balances the charge of free ions and can bear a carbon chain that can attach to SiO2 nanoparticles. Synthetic SiO2-MIM+ was combined either with bis(trifluoromethanesulfonyl) imide (NTf2−) or hexafluorophosphate (PF6−), and synthetic SiO2-NTf2− was combined with either 1-butyl-3-methylimidazolium (BMIM+) and tetra- butylammonium (NBu4+)(Fig. 1a).

Figure 2 shows the reaction steps for synthesizing SiO2-grafted ILs, namely, SiO2-IL-NMF (1), SiO2-IL-PF6 (2), SiO2-IL-BMIM (3), and SiO2-IL-NBu4 (4) (see methods). The main issue of this synthetic method was the preparation of key intermediate products, particularly SiO2-MIM-Cl (5) and SiO2-NMF-Li (6) for the attachment of ions (MIM+ and NTf2−) to SiO2 nanoparticles. To obtain compound 9, we actuated a quaternization reaction between (3-chloropropyl)trimethoxysilane (7) and 1-methylimidazole (8). The produced compound 9 was subsequently attached to the SiO2 nanoparticles by a condensation reaction for the production of SiO2-MIM-Cl (5). Compound 5 was subjected to an ion exchange with LiNMF2 (10) and LiPF6 (11) and successfully converted into SiO2-IL-NMF (1) and SiO2-IL-PF6 (2), respectively. For the preparation of SiO2-NMF-Li (6), compound 12 was first converted into compound 13 via trifluoromethanesulfonylation, followed by lithiation. Then, compound 13 was attached to the SiO2 nanoparticles for SiO2-
NTf-Li (6) production. Lithium ion (Li+) in SiO2-NTf-Li (6) was substituted with BMIM+ (14) or NBu4+ (15) through ion exchange for SiO2-IL-BMIM (3) and SiO2-IL-NBu4 (4) production.

The chemical structures and purity of the synthesized SiO2-grafted ILs were confirmed by 1H NMR and 19F NMR. The results indicated that MIM+ and NTf− were successfully attached to the SiO2 nanoparticles (Supplementary Fig. 3) and inductively coupled plasma optical emission spectroscopy (see Supplementary Information) results verified that the absence of Cl, Br, or Li in the SiO2-grafted ILs, suggesting that excess salt (LiCl or LiBr) was completely removed after ion exchange. The above measurements confirmed that only one type of ion was free in each SiO2-grafted IL. The IR spectra further demonstrated the existence of characteristic bands for the SiO2-grafted ILs (Supplementary Fig. 14), indicating the successful grafting of IL molecules on the SiO2 nanoparticles. The ion concentrations (the ratio of the mole number of ions to the mass of the corresponding ILs or organic salts (BMIM-NTf2, BMIM-PF6, NBu4-NTf2, and NBu4-PF6)) dissolved in anhydrous propylene carbonate (PC) with the same concentration of 0.25 M were used as electrolytes (Supplementary Fig. 16). The electrochemical behavior of AC electrodes in electrolytes was characterized in a closed three-electrode system. Figure 3 shows the cyclic voltammetry (CV) curves of the YP-50F electrode in four SiO2-grafted IL electrolytes at the same scan rate (5 mV s−1). The CV curves of SiO2-IL-BMIM within different operating potential windows (Fig. 3a), which should actually exhibit the sorption property of BMIM+ because only it can freely enter the pores of YP-50F, all showed that the specific capacitance rapidly decreased when the electrode was positively polarized to ~0.9 V/ref (the maximum slope was around this potential). This rapid decrease in capacitance indicated that the upper acting potential for the capacitance contribution of BMIM+ was ~0.9 V/ref (Supplementary Note1, Supplementary Figs. 17 and 18). The CV curves of SiO2-IL-NBu4 exhibited a similar feature (Fig. 3c). Thus, the upper acting potential for the capacitance contribution of NBu4+ was ~1.0 V/ref. The rapid decrease in capacitance was also observed in the CV curves of SiO2-IL-NTf2 (Fig. 3b) and SiO2-IL-PF6 (Fig. 3d), but the decrease occurred at negatively polarized directions (~0.1 V/ref for SiO2-IL-NTf2 and 0.1 V/ref for SiO2-IL-PF6). The lower acting potentials for the capacitance contributions of anions were ~0.1 V/ref for NTf2− and ~0.1 V/ref for PF6−. Comparisons between the CV curves of two cations with the same operating potential windows and between those of two anions were conducted. The results showed that the capacitance contribution of BMIM+ was larger than that of NBu4+ for the YP-50F electrode, and that of NTf2− was larger than that of PF6− (Supplementary Note1).

**Electrochemical measurements.** A commercially available AC (YP-50F, Kuraray Chemical, Japan) was used as electrode (Supplementary Fig. 1). Four synthesized SiO2-grafted ILs and the corresponding ILs or organic salts (BMIM-NTf2, BMIM-PF6, NBu4-NTf2, and NBu4-PF6) dissolved in anhydrous propylene carbonate (PC) with the same concentration of 0.25 M were used as electrolytes (Supplementary Fig. 16). The electrochemical behavior of AC electrodes in electrolytes was characterized in a closed three-electrode system. Figure 3 shows the cyclic voltammetry (CV) curves of the YP-50F electrode in four SiO2-grafted IL electrolytes at the same scan rate (5 mV s−1). The CV curves of SiO2-IL-BMIM within different operating potential windows (Fig. 3a), which should actually exhibit the sorption property of BMIM+ because only it can freely enter the pores of YP-50F, all showed that the specific capacitance rapidly decreased when the electrode was positively polarized to ~0.9 V/ref (the maximum slope was around this potential). This rapid decrease in capacitance indicated that the upper acting potential for the capacitance contribution of BMIM+ was ~0.9 V/ref (Supplementary Note1, Supplementary Figs. 17 and 18). The CV curves of SiO2-IL-NBu4 exhibited a similar feature (Fig. 3c). Thus, the upper acting potential for the capacitance contribution of NBu4+ was ~1.0 V/ref. The rapid decrease in capacitance was also observed in the CV curves of SiO2-IL-NTf2 (Fig. 3b) and SiO2-IL-PF6 (Fig. 3d), but the decrease occurred at negatively polarized directions (~0.1 V/ref for SiO2-IL-NTf2 and 0.1 V/ref for SiO2-IL-PF6). The lower acting potentials for the capacitance contributions of anions were ~0.1 V/ref for NTf2− and ~0.1 V/ref for PF6−. Comparisons between the CV curves of two cations with the same operating potential windows and between those of two anions were conducted. The results showed that the capacitance contribution of BMIM+ was larger than that of NBu4+ for the YP-50F electrode, and that of NTf2− was larger than that of PF6− (Supplementary Note1).

**Fig. 1** Schematic of the strategy for respectively characterizing the charging behavior of cations and anions of ionic liquids in electrochemical double-layer capacitors (EDLCs). a Structures of cations, anions, and silica nanoparticle-grafted ions. b Transmission electron micrograph of silica nanoparticles with a uniform diameter of 7 nm. Scale bar, 50 nm. c Pore size distributions of two activated carbons, which indicate that the pore sizes in two activated carbons are smaller than the diameter of silica nanoparticles. d Schematic of charge storage of activated carbon electrodes during polarization in different types of ionic liquids: silica nanoparticle-grafted cations and free anions (top), silica nanoparticle-grafted anions and free cations (middle), conventional cations and anions (bottom). Big blue balls represent silica nanoparticles, small wine balls represent cations, and green balls represent anions.
The difference may be attributed to the differences between the compared ions with respect to size and chemical structure, which may have affected the interface interaction between the ions and pore surfaces of carbon electrodes. Meanwhile, some studies reported that one type ions can solely contribute to charge storage mechanisms. The CV curves of SiO₂-IL-NTf₂ and SiO₂-IL-PF₆ were similar to that of another commercial AC (YP-17, Kuraray Chemical, Japan) electrode in tetraoctylammonium tetrafluoroborate (TOA-BF₄) IL, in which the charge at the negatively polarized electrode rapidly decreases because the bulky 1.12 nm TOA⁺ cations are inaccessible to most of the carbon pores. Basing on this similarity, we concluded that ions attached to SiO₂ nanoparticles were indeed restricted out of the pores of YP-50F during the charging process.

We summed the CV curves of SiO₂-IL-BMIM and SiO₂-IL-NTf₂, SiO₂-IL-BMIM and SiO₂-IL-PF₆, SiO₂-IL-NBu₄ and SiO₂-IL-NTf₂, and SiO₂-IL-NBu₄ and SiO₂-IL-PF₆ to obtain the summed CV curves of the YP-50F electrode in four organic electrolytes (BMIM-NTf₂, BMIM-PF₆, NBu₄-NTf₂, and NBu₄-PF₆), as shown in Fig. 4a-d. The summed CV curves (blue dotted lines) represented a perfect state, in which all cations and anions fully contributed their capacitance. On the two sides of each highly polarized region, a purely adsorptive mechanism should be observed. In particular, only the counter-ions contributed capacitance (light red, orange, blue, and green regions). Taking Fig. 4a as an example, the capacitance only originated from the contribution of BMIM⁺ at a negatively polarized potential window (below −0.1 V/ref); and at the high positively polarized...
potential window (above 0.9 V/ref) the capacitance was only contributed by NTf$_2^\text{−}$. At a middle potential window of −0.1 to 0.9 V/ref (gray region), both BMIM$^+$ and NTf$_2^\text{−}$ presented charge storage, and the capacitance value of the summed CV curve was larger than that of the CV curve in SiO$_2$-IL-BMIM or SiO$_2$-IL-NTf$_2$. However, is it true? To determine whether the two ions at the middle region can promote each other and thus exhibit summed capacitance, we tested the actual CV curves of the four.

---

**Fig. 3** Cyclic voltammetry (CV) curves of YP-50F electrode in four SiO$_2$-grafted ILs with the same concentration of 0.25 M in propylene carbonate (PC). a SiO$_2$-IL-BMIM, b SiO$_2$-IL-NTf$_2$, c SiO$_2$-IL-NBu$_4$, and d SiO$_2$-IL-PF$_6$. The curves were scanned within different operating potential windows with the same scan rate of 5 mV s$^{-1}$.

**Fig. 4** Comparison of the summed CV curves with the real CV curves. Summed cyclic voltammetry (CV) curves of YP-50F electrode in four electrolytes by summing the CV curves of YP-50F electrode in four SiO$_2$-grafted ILs shown in Fig. 3: a SiO$_2$-IL-BMIM and SiO$_2$-IL-NTf$_2$, b SiO$_2$-IL-BMIM and SiO$_2$-IL-PF$_6$, c SiO$_2$-IL-NBu$_4$ and SiO$_2$-IL-NTf$_2$, d SiO$_2$-IL-NBu$_4$ and SiO$_2$-IL-PF$_6$. Summed CV curves and real CV curves of YP-50F electrode in four corresponding conventional organic electrolytes: e BMIM-NTf$_2$, f BMIM-PF$_6$, g NBu$_4$-NTf$_2$, and h NBu$_4$-PF$_6$. All tested CV curves were scanned within the operating potential window of −0.8 V to 1.2 V/ref with the same scan rate of 5 mV s$^{-1}$. The organic electrolytes had the same concentration of 0.25 M in propylene carbonate (PC).
and b voltammetry (CV) curve with a scan rate of 5 mV s⁻¹ (Supplementary Table 1). The decrease may be caused by the restricted movement of the free ions of the SiO₂-grafted ILs perm-selective behavior during polarization. Cyan solid line represents the experimental ion population change. Red dashed line is the theoretical ion population change based on SADC in SiO₂-IL-BMIM and SiO₂-IL-NTf₂ ILs, both of which selected as study sample. Figure 5a, b show the CV curves of homemade sodium alginate-derived AC (denoted as SADC) was further verified on the basis of the acting potential of each SiO₂-grafted IL shown in Fig. 3). The summed CV curves represented the real overall sorption behavior of cations and anions on carbon surfaces, and the actual CV curves represented the real overall sorption behavior of cations and anions on the same carbon surfaces. Therefore, the comparison results indicated that the cations and anions competed with each other within the middle region. In addition, the capacitance of the summed curves was smaller than that of the conventional electrolytes upon the reversal of the potential possibly because of the decreased ionic conductivity of the SiO₂-grafted ILs (Supplementary Table 1). The decrease may be caused by the restricted movement of the free ions of the SiO₂-grafted ILs because of the nearly immobile SiO₂ nanoparticles.

After separately monitoring the charging behavior of cations and anions of ILs using YP-50F electrode as the study subject, we further verified the feasibility of this strategy for other ACs. The homemade sodium alginate-derived AC (denoted as SADC) was selected as study sample. Figure 5a, b show the CV curves of SADC in SiO₂-IL-BMIM and SiO₂-IL-NTf₂ ILs, both of which had the same concentration of 0.25 M in PC. Figure 5c shows the summed and real CV curves of the SADC in the BMIM-NTf₂/PC electrolyte. Similar CV shapes appeared for the SADC electrode. BMIM⁺ dominated at the potential below −0.5 V/ref, NTf₂⁻ dominated at the potential above 1.2 V/ref, and BMIM⁺ and NTf₂⁻ competed at the middle potential window of −0.5 to 1.2 V/ref. The results of the CV comparison between the YP-50F and SADC electrodes (Supplementary Fig. 20) indicated that latter had higher capacitance than former in the BMIM-NTf₂ electrolyte system. It because the SADC had higher Brunauer–Emmett–Teller surface area than the YP-50F (Supplementary Figs. 1 and 2).

As mentioned before, changes in electrode mass during dynamic ion charging can be measured in real time through EQCM. Thus, in situ EQCM investigation was conducted to study the specific charge mechanisms of cations and anions within the competitive potential window indicated above. Figure 6a shows the CV curve and the simultaneous mass change (Δm; calculated from the frequency response change of EQCM experiment through Sauerbrey’s equation (see Supplementary Information)) of YP-50F-coated quartz (as working electrode; Supplementary Note 2, Supplementary Fig. 22) in a BMIM-NTf₂/PC electrolyte within an operating potential window of −0.2 to 0.9 V/ref. Potential window was selected by a chronoamperometry test (Supplementary Note 3, Supplementary Figs. 23 and 24). Moreover, when the YP-50F-coated quartz electrode was cycled between −0.2 V and 0.9 V/ref, the resonance width change (ΔW) should be much smaller than the simultaneous resonance frequency change (Δf; Supplementary Note 4, Supplementary Fig. 25). In Fig. 6a, at potential scans ranging from 0.9 V/ref...
to −0.2 V/ref, the mass change (olive line) typically showed a V shape. At the subsequent potential back scanning from −0.2 V/ref to 0.9 V/ref, the mass change (blue line) was nearly coincidental with the previous one, indicating the reversibility of the current experiment. The potential of zero mass change (pzmc), which corresponded to the minimum mass change, was close to 0.34 V/ref. The evaluated potential of zero charge (pzc) of 0.27 V/ref was shifted to the left with respect to pzmc (Supplementary Fig. 21).

Figure 6b shows that the ion population change ($\Delta Q$) is a function of charge density ($\Delta Q = $ calculated by integration of the related CV). The cyan line represents the experimental ion population change obtained by dividing the mass change by the molecular weight of the ion, and the red dashed line is the theoretical ion population change calculated by assuming adsorption of solely counter-ions with the use of Faraday's law (see Supplementary Information). During the negative polarization from pzc ($\Delta Q < 0$), the experimental ion population change was nearly equal to the theoretical one, implying that the charge on the negatively polarized electrode was solely balanced by the principle adsorption of counter-ions (BMIM$^+$), and no solvent was involved$^{37,38,43}$. The shift of pzc to the left with respect to pzmc indicated that desorption of co-ions (BMIM$^+$) played a dominant role in the potential between pzc and pzmc (Supplementary Fig. 21).

The EQCM results were further combined with the results obtained in the CV curves of SiO$_2$-grafted ILs (SiO$_2$-IL-BMIM (red curve), SiO$_2$-IL-NH$_2$FB (green curve)) to yield an in-depth understanding of the charging mechanism of carbon YP-50F in BMIM-NTf$_2$/PC (Fig. 7). At highly negatively and positively polarized regions (below −0.1 V/ref and above 0.9 V/ref), only the adsorption of the counter-ions (NTf$_2^-$) was involved.

**Discussion**

In summary, we demonstrated a method to separately monitor cations (BMIM$^+$, NBu$_4^+$) and anions (NTf$_2^-$, PF$_6^-$) in AC pores by utilizing four SiO$_2$-grafted ILs, which were successfully prepared by organic synthesis. The charging behaviors of BMIM$^+$, NBu$_4^+$, NTf$_2^-$, and PF$_6^-$ at different potential states can be directly measured through conventional CV tests and by ensuring that only one type of ion enters the AC pores. The CV results of cations and anions indicated that capacitance originated from the contribution of the counter-ions or from the competition between counter-ions and co-ions, which were determined by the polarization of AC electrodes. An extensive understanding of the detailed charge storage mechanism of AC in BMIM-NTf$_2$ system was achieved by further combining the relative results of BMIM$^+$ and NTf$_2^-$ with the data obtained from the EQCM experiment. The perm-selective behavior alone was observed at the highly polarized potential regions (below −0.1 V/ref and above 0.9 V/ref), whereas perm-selective and ion swapping behaviors were both observed at the low polarized potential regions (below −0.1 V/ref and above 0.9 V/ref), indicating the respective characterization of charging behavior of cations and anions of ILs in ACs. We can imagine the characterization of various types of ions can be achieved by utilizing the corresponding SiO$_2$-grafted ILs. Our work is of great significance to the rational choice of IL electrolytes and efficient construction of high-performance EDLCs.

**Methods**

**Preparation of silica nanoparticle-grafted ionic liquids.** SiO$_2$-MIM-Cl (5). 1-methylimidazole (8, 8.0 mL, 0.1 mmol) was added in a solution of 3-chloropropyltrimethoxysilane (7, 18.2 mL, 0.1 mmol) in dimethylformamide (DMF, 120 mL) and the mixture was stirred at 80 °C for 48 h. After the reaction was completed, the solvent was evaporated under vacuum. The resulting viscous liquid was dissolved in H$_2$O and the organic byproducts were extracted with ether (Et$_2$O) and dichloromethane (CH$_2$Cl$_2$). The aqueous phase was evaporated under vacuum and the product 9 was obtained as yellow oil. Subsequently, an aqueous suspension of silica nanoparticles (200 mL, 2.5 wt%) was added in an aqueous solution of 9 (5 mL, 1.0 mol/L) slowly. The mixture was stirred at 80 °C for 12 h to afford SiO$_2$-MIM-Cl (5) as a white suspension without further purification.

SiO$_2$-NTf$_2$-Li (6). The trifluoromethanesulfonyl anhydride (TF$_2$O, 16.9 mL, 0.1 mmol) was slowly added in a solution of 3-trimethoxysilylprop-1-amine (12, 17.5 mL, 0.1 mmol) and triethylamine (Et$_3$N, 28 mL, 0.2 mmol) in dried CH$_2$Cl$_2$ (150 mL) at −78 °C under dry argon atmosphere. The mixture was stirred for 1 h and then heated to room temperature. An aqueous of potassium hydroxide (KOH, 17.1 g, 0.3 mmol) was then added in this mixture and the resulting organic byproducts were extracted with CH$_2$Cl$_2$. The aqueous phase was neutralized with hydrochloric acid (HCl, 80 mL, 4 mol/L) and extracted with ethyl acetate. The organic phase was dried by magnesium sulfate (MgSO$_4$) and then concentrated to a stock solution.

---

**Fig. 7** Combination of electrochemical quartz crystal microbalance (EQCM) data with the cyclic voltammetry (CV) curves shown in Fig. 4a.

Capacitance (F g$^{-1}$) vs. Potential (V vs. Ag) for SiO$_2$-IL-BMIM (red curve), SiO$_2$-IL-NH$_2$FB (green curve) at different potential states can be determined by integrating the area under the CV curve.

The EQCM experiment revealed that at the low positively polarized region (0.27 V/ref to 0.9 V/ref, domains II and III), the adsorption of counter-ions (NTf$_2^-$) and desorption of co-ions (BMIM$^+$) both contributed capacitance, and the role of counter-ion (NTf$_2^-$) adsorption became evident as the polarization degree increased. At the highly positively polarized region (above 0.9 V/ref, domain IV), only the adsorption of the counter-ions (NTf$_2^-$) was involved.
afford a colorless oil. This oil was dissolved in anhydrous acetonitrile (CH₃CN, 150 mL) and lithium hydride (LiH, 1.2 g, 0.15 mmol) was then added in the solution slowly at 0 °C. The resulting solid byproducts and excess LiH were removed by filtration. After the solvent was evaporated under vacuum, the product 13 was obtained as white solid. Subsequently, an aqueous suspension of silica nanoparticles (200 mL, 2.5 wt%) was added in a solution of 13 (15 mL, 1.0 mol/L in H₂O) slowly. The mixture was stirred at 80 °C for 12 h to afford SiO₂-MIM-Cl (6) as a white suspension without further purification.

SiO₂-IL-NTf₂ (1). The suspension of SiO₂-MIM-Cl (5) was added in an aqueous solution of LiNTf₂ (10, 1.05 equiv. to 9 in previous step). After fully mixing, the precipitating precipitation was separated by centrifugation. The solid product was washed by washing with acetone/H₂O (v/v = 3/2) and centrifugation. The final traces of H₂O were removed by lyophilized under vacuum to afford the product SiO₂-IL-NTf₂ (1).

SiO₂-IL-PFe₃ (2). The suspension of SiO₂-MIM-Cl (5) was added in an aqueous solution of LiPFe₃ (11, 1.05 equiv. to 9 in previous step). After fully mixing, the precipitating precipitation was separated by centrifugation. The solid product was washed by washing with acetone/H₂O (v/v = 3/2) and centrifugation. The final traces of H₂O were removed by lyophilized under vacuum to afford the product SiO₂-IL-PFe₃ (2).

Material characterization. ¹H NMR and ¹⁹F NMR spectra were recorded in d₅-DMSO solution on a Bruker 400 MHz spectrometer. The spectral data were reported in ppm and calibrated by using DMSO (2.5 ppm) as internal reference for ¹H NMR. The nitrogen adsorption-desorption isotherm was measured on an ASAP 2020 M porosimeter (Micrometrics) at −77 K. The specific surface area (SSA) was calculated using the Brunauer–Emmett–Teller (BET) method and the pore size distribution (PSD) was calculated from the isotherm using the Barrett–Joyner–Halenda (BJH) method. Transmission electron microscopy (TEM) was conducted using a JEOL 2100 FEG microscope at 200 keV. Scanning electron microscope (SEM) was conducted using a JEOL JSM 6701 F microscope. Energy dispersive X-ray spectroscopy (EDS) was conducted using a JSM-6501LV microscope. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted using a Leeman Prodigy7 spectrometer. Fourier transform infrared (FTIR) spectra were recorded using a Nexus 870 FTIR spectrometer. Thermo-gravimetric analysis (TGA) was carried out using a STA 449 C thermal analyzer at a heating rate of 10 °C/min in air atmosphere. The electrical conductivity of IL electrolytes was measured by using a Mettler Toledo F30 FiveEasy conductivity meter.

Electrochemical measurements. Electrochemical CV tests were carried out using an electrochemical workstation (CHI440C, Shanghai, China) in a closed three-electrode system, assembled in a glovebox under argon, with a silver disk as the quasi-reference electrode, a platinum foil (1 x 3 cm²) as the counter electrode and a carbon electrode as the working electrode. The carbon electrodes were prepared from YP-50F, 90 wt% carbon loading was 25–50 µg cm⁻², which was then dried at 60 °C under vacuum (details see Supplementary Information). The corresponding CV tests were carried out at a scan rate of 5 mV s⁻¹ with simultaneous recording of the quartz resonance frequency. Before recording the data, each CV test was firstly cycled three times to make sure the system reached a steady state.

Received: 17 April 2017 Accepted: 10 November 2017

Published online: 19 December 2017

References

1. Miller, J. R. & Simon, P. Electrochemical capacitors for energy management. Science 321, 651–652 (2008).
2. Simon, P. & Gogotsi, Y. Materials for electrochemical capacitors. Nat. Mater. 7, 845–854 (2008).
3. Winter, M. & Brodd, R. J. What are batteries, fuel cells, and supercapacitors? Adv. Energy Mater. 4, 4245–4270 (2014).
4. Yan, J., Wang, Q., Wei, T. & Fan, Z. Recent advances in design and fabrication of electrochemical supercapacitors with high energy densities. Adv. Energy Mater. 4, 1300816 (2014).
5. Yang, Z. et al. Recent advancement of nanostuctured carbon for energy applications. Chem. Rev. 115, 5159–5223 (2015).
6. Li, H. et al. Capacitance of carbon-based electrical double-layer capacitors. Nat. Commun. 5, 3317 (2014).
7. Béguin, F., Presser, V., Balducci, A. & Frackowiak, E. Carbons and electrolytes for advanced supercapacitors. Adv. Mater. 26, 2219–2251 (2014).
8. Zhong, C. et al. A review of electrolyte materials and compositions for electrochemical supercapacitors. Chem. Soc. Rev. 44, 7484–7539 (2015).
9. Armand, M., Endres, F., MacFarlane, D. R., Ohno, H. & Scrosati, B. Ionic-liquid materials for the electrochemical challenges of the future. Nat. Mater. 8, 621–629 (2009).
10. Watanabe, M. et al. Application of ionic liquids to energy storage and conversion materials and devices. Chem. Rev. 117, 7190–7239 (2017).
11. MacFarlane, D. R. et al. Energy applications of ionic liquids. Energy Environ. Sci. 7, 232–250 (2014).
12. Fedorov, M. V. & Kornyshev, A. A. Ionic liquids at electrochemical interfaces. J. Phys. Chem. C. 114, 2978–3036 (2014).
13. Adam, D. Clean and green... but are they mean? Nature 407, 938–940 (2000).
14. Van Aken, K. L., Beidaghi, M. & Gogotsi, Y. Formulation of ionic-liquid electrolyte to expand the voltage window of supercapacitors. Angew. Chem. Int. Ed. 54, 4806–4809 (2015).
15. Shi, M., Kou, S.-Y. & Yan, X. Engineering the electrochemical capacitive properties of graphene sheets in ionic-liquid electrolytes by correct selection of anions. ChemSusChem 7, 3053–3062 (2014).
16. Hayes, R., Warr, G. G. & Atkin, R. Structure and nanostructure in ionic liquids. Chem. Rev. 115, 6357–6426 (2015).
17. Zhang, S., Zhang, J., Zhang, Y. & Deng, Y. Nanoconfined ionic liquids. Chem. Rev. 117, 6755–6833 (2017).
18. Vatanavan, I., Vatanavan, M. & Bedrov, D. Non-faradaic energy storage by room temperature ionic liquids in nanoporous electrodes. ACS Nano 9, 5960–6107 (2015).
19. Jackel, N., Simon, P., Gogotsi, Y. & Presser, V. Increase in capacitance by subnanometer pores in carbon. ACS Energy Lett. 1, 1262–1265 (2016).
20. Lian, C. et al. Enhancing the capacitive performance of electric double-layer capacitors with ionic liquid mixtures. ACS Energy Lett. 1, 21–26 (2016).
21. Varanasi, S. R. & Bhattacharya, K. Optimal electrode mass ratio in nanoporous carbon electrochemical supercapacitors. J. Phys. Chem. C 120, 27925–27933 (2016).
22. Forse, A. C., Merlet, C., Griffin, J. M. & Grey, C. P. New perspectives on the charging mechanisms of supercapacitors. J. Am. Chem. Soc. 138, 5731–5744 (2016).
23. Salanne, M. et al. Efficient storage mechanisms for building better supercapacitors. Nat. Energy 1, 16070 (2017).
24. Wu, P., Huang, J., Meunier, V., Sumper, B. G. & Qiao, R. Complex capacitance scaling in ionic liquids-filled nanopores. ACS Nano 5, 9044–9051 (2011).
25. Raitpur, N. N., Monk, J. & Hung, F. R. Structure and dynamics of an ionic liquid confined inside a charged slit graphene nanopore. J. Phys. Chem. C. 116, 14504–14513 (2012).
26. Merlet, C. et al. On the molecular origin of supercapacitance in nanoporous carbon electrodes. Nat. Mater. 11, 306–310 (2012).
27. Merlet, C. et al. Highly confined ions store charge more efficiently in supercapacitors. Nat. Commun. 4, 2701 (2013).

Data availability. All relevant data supporting the findings of this study are available from the authors on request.
28. Kondrat, S., Wu, P., Qiao, R. & Kornyshev, A. A. Accelerating charging dynamics in subnanometre pores. Nat. Mater. 13, 387–393 (2014).
29. Kondrat, S. & Kornyshev, A. A. Presuing a spring: what does it take to maximize the energy storage in nanoporous supercapacitors? Nanoscale Horiz. 1, 45–52 (2016).
30. Kondrat, S. & Kornyshev, A. Charging dynamics and optimization of nanoporous supercapacitors. J. Phys. Chem. C 117, 12399–12406 (2013).
31. Richey, F. W., Dyatkin, B., Gogotsi, Y. & Elabd, Y. A. Ion dynamics in porous carbon electrodes in supercapacitors using in situ infrared spectroelectrochemistry. J. Am. Chem. Soc. 135, 12818–12826 (2013).
32. Richey, F. W. & Elabd, Y. A. In situ molecular level measurements of ion dynamics in an electrochemical capacitor. J. Phys. Chem. Lett. 3, 3297–3301 (2012).
33. Boukhalfa, S. et al. In situ small angle neutron scattering revealing ion sorption in microporous carbon electrical double layer capacitors. ACS Nano 8, 2495–2503 (2014).
34. Bafuñejo, J. L. et al. Densefication of ionic liquid molecules within a hierarchical nanoporous carbon structure revealed by small-angle scattering and molecular dynamics simulation. Chem. Mater. 26, 1144–1153 (2014).
35. Boukhalfa, S., He, L., Mehmenkeno, Y. B. & Yushin, G. Small-angle neutron scattering for in situ probing of ion adsorption inside micropores. Angew. Chem. Int. Ed. 52, 4618–4622 (2013).
36. Levi, M. D., Salitra, G., Levy, N., Aurbach, D. & Maier, J. Application of a quartz-crystal microbalance to measure ionic fluxes in microporous carbons for energy storage. Nat. Mater. 8, 872–875 (2009).
37. Levi, M. D., Sigalov, S., Aurbach, D. & Daikkin, L. In situ electrochemical quartz crystal admittance methodology for tracking compositional and mechanical changes in porous carbon electrodes. J. Phys. Chem. C 117, 14876–14889 (2013).
38. Tsai, W. Y., Taberna, P. L. & Simon, P. Electrochemical quartz crystal microbalance (EQCM) study of ion dynamics in nanoporous carbons. J. Am. Chem. Soc. 136, 872–878 (2014).
39. Levi, M. D. et al. Electrochemical quartz crystal microbalance (EQCM) studies of ions and solvents insertion into highly porous activated carbons. J. Am. Chem. Soc. 132, 13220–13222 (2010).
40. Sigalov, S., Levi, M. D., Salitra, G., Aurbach, D. & Maier, J. EQCM as a unique tool for determination of ionic fluxes in microporous carbons as a function of surface charge distribution. Electrochem. Commun. 12, 1718–1721 (2010).
41. Levi, M. D. et al. In situ porous structure characterization of electrodes for energy storage and conversion by EQCM-D: a review. Electrochim. Acta 232, 271–284 (2017).
42. Levi, M. D., Sigalov, S., Salitra, G., Aurbach, D. & Maier, J. The effect of specific adsorption of cations and their size on the charge-compensation mechanism in carbon micropores: the role of anion desorption. Chem. Phys. Chem. 12, 854–862 (2011).
43. Shipigl, N. et al. Novel in situ multiharmonic EQCM-D approach to characterize complex carbon pore architectures for capacitive deionization of brackish water. J. Phys. Condens. Matter 28, 114001 (2016).
44. Griffin, J. M. et al. In situ NMR and electrochemical quartz crystal microbalance techniques reveal the structure of the electrical double layer in supercapacitors. Nat. Mater. 14, 812–819 (2015).
45. Blanc, F., Leskes, M. & Grey, C. P. In situ solid-state NMR spectroscopy of electrochemical cells: batteries, supercapacitors, and fuel cells. Acc. Chem. Res. 46, 1952–1963 (2013).
46. Deschamps, M. et al. Exploring electrolyte organization in supercapacitor electrodes with solid-state NMR. Nat. Mater. 12, 351–358 (2013).
47. Forse, A. C. et al. NMR study of ion dynamics and charge storage in ionic liquid supercapacitors. J. Am. Chem. Soc. 137, 7231–7242 (2015).
48. Forse, A. C. et al. Direct observation of ion dynamics in supercapacitor electrodes using in situ diffusion NMR spectroscopy. Nat. Energy 2, 16216 (2017).
49. Wang, H. et al. In situ NMR spectroscopy of supercapacitors: insight into the charge storage mechanism. J. Am. Chem. Soc. 135, 18968–18980 (2013).
50. Wang, H. et al. Real-time NMR studies of electrochemical double-layer capacitors. J. Am. Chem. Soc. 133, 19270–19273 (2011).
51. Lu, Y., Moganty, S. S., Schafer, J. L. & Archer, L. A. Ionic liquid-nanoparticle hybrid electrolytes. J. Mater. Chem. 22, 4066–4072 (2012).
52. Lu, Y., Korf, K., Kambe, Y., Tu, Z. & Archer, L. A. Ionic-liquid-nanoparticle hybrid electrolytes: applications in lithium metal batteries. Angew. Chem. Int. Ed. 53, 488–492 (2014).

Acknowledgements

This work was supported by the National Nature Science Foundations of China (21573265 and 21673263).

Author contributions

X.B.Y. designed this work; Q.Y.D. carried out the organic synthesis and electrochemical experiments; B.J.Y. and J.W.L. made sodium alginate-derived AC; X.B.Y. and Q.Y.D. wrote the paper and analyzed the results. All authors contributed to the discussion of the results.

Additional information

Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-017-02152-5.

Competing interests: The authors declare no competing financial interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2017