

Supporting Information
for

Charge transfer and electrical double layer of an amphiphilic protic ionic liquid
in bulk and when confined in nanopores

authored by
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I. Information on the porous silica thin film

Materials

As silica precursor tetraethyl orthosilicate (TEOS, 98%, Sigma-Aldrich) was used, while ethanol (EtOH, 99.5%, Solveco) was used as the co-solvent, sodium nitrate (NaNO₃, 99%, Sigma-Aldrich) as the electrolyte's salt, and 0.1 M HCl in aqueous solution (HCl_(aq), VWR) to adjust the pH. Hexadecyltrimethylammonium bromide (CTAB, 99%, Sigma Aldrich) was used as silica template. For the extraction of the templating CTAB, an ethanol solution of 0.1 M HCl was used that was prepared by dilution of nominally 2.5 M HCl in ethanol (HCl_(EtOH), Alfa Aesar). The redox-probes for cyclic voltammetry were hexaammineruthenium(III) chloride ([Ru(NH₃)₆]Cl₃, 98%, Sigma Aldrich), potassium hexa-cyanoferrate(III) (K₃[Fe(CN)₆], 99.0%, Sigma-Aldrich) and α -methylferrocenemethanol (C₁₂H₁₄FeO, 97%, Sigma-Aldrich). All aqueous solutions were prepared with Milli-Q water.

Synthesis

The CTAB-templated mesoporous silica thin films were synthesized *via* the electrochemically-assisted self-assembly (EASA) method (1). First, a solution was prepared containing 100 mM TEOS, 0.1 M NaNO₃ in 40 ml ethanol:water (1:1) mixture with CTAB added at a 0.32 CTAB/TEOS ratio (reported in mol/mol). The solution was adjusted to pH 3 with 0.1 M HCl and stirred for 2.5 h at room temperature to let proceed the pre-hydrolysis of TEOS. The potentiostatic deposition over an indium tin oxide electrode (ITO, surface resistivity 8–12 Ω , Delta Technologies) was carried out in a three-electrode system in which the ITO functioned as the cathodic working electrode, silver wire as the pseudo-reference electrode and stainless steel as the counter electrode. The potential was applied using a Gamry Interface1000E potentiostat. The deposition of a silica film on ITO could be observed at an applied voltage of – 1.3 V, while the deposition time was set to 25 s. After deposition, the films were rinsed with water and aged at 130 °C in a vacuum oven, overnight. After aging, extraction of the CTAB was carried out by immersing the deposited film into a solution of 0.1 M HCl in ethanol for 20 min, followed by rinsing with pure ethanol and drying in a vacuum oven for 2 h at 90 °C.

Characterization methods

To determine the permeability of the silica films, cyclic voltammetry (CV) was used as described in reference (2) with the only difference that the used potentiostat was a Gamry Interface1000E instrument. The transmission-reflection IR (Infrared) spectra and the GISAXS (gazing-incidence small-angle X-ray scattering) patterns were collected and processed according to reference (2).

(1) Despas, C., Vodolazkaya, N. A., Ghanbaja, J., Walcarius, A.; Preparation of ordered and oriented mesoporous silica thin films bearing octyl or hexadecyl groups by electrochemically assisted self-assembly and evaluation of their transport properties *J Solid State Electrochem* (2015) 19:2075–2085 DOI 10.1007/s10008-014-2726-2

(2) S. Vavra, N. Vilá, A. Lotsari, A. Walcarius, A. Martinelli; An imidazolium ionic liquid as effective structure-directing agent for the fabrication of silica thin films with vertically aligned nanochannels, *Microporous and Mesoporous Materials* (2020). doi:10.1016/j.micromeso.2020.110407.

Extraction

To avoid possible dissolution of the silica film in the acidic extraction solution, a control sample (deposited in the same batch) was used to verify the extraction process. On Figure S1 it is shown that for the positive $[\text{Ru}(\text{NH}_3)_6]^{3+}$ and negative $[\text{Fe}(\text{CN})_6]^{3-}$ redox probe the film is impermeable indicating good, intact coverage of the control film. In contrary, the neutral FcMeOH probe can reach the electrode resulting in Faradic currents, which can be understood by the probe being able to dissolve in the lyophilic phase of the assembled alkyl chains of the CTAB located inside the channel-like pores. After 20 min of extraction of the CTAB, the channels are permeable for the positive and neutral redox probes, but not for the negative one due to the repulsive negative charge of the silica walls. Again, the latter demonstrates the good coverage of the control film. When the control sample was soaked in the extraction solution for further 10 min, the properties of the film had not changed showing its chemical stability in acidic conditions. Also, the IR spectra of the control film at the different stages of the extraction, Figure S2, prove that 20 min of extraction is enough to remove the CTAB since the area of the absorption peaks assigned to the C-H stretching modes of the alkyl chains drastically decrease with no further changes for prolonged soaking times in the extraction solution.

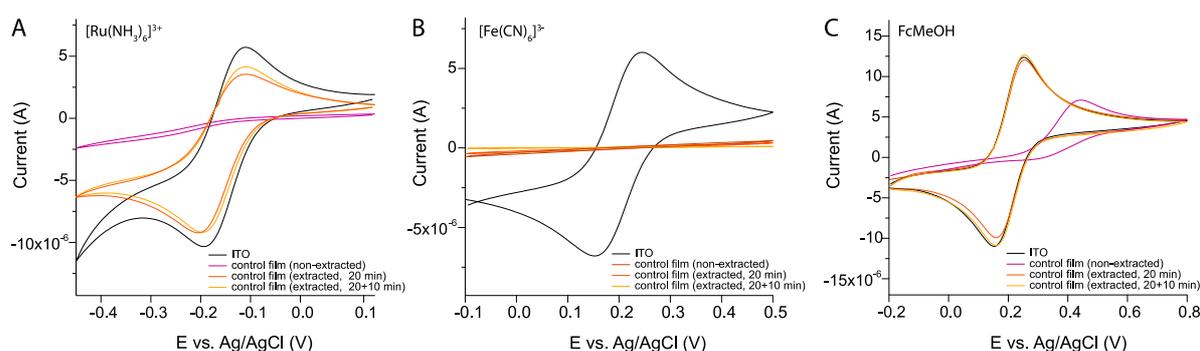


Figure S1. Cyclic voltammetric curves recorded with a positive redox-probe $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ solution (A), a negative redox-probe $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution (B), and a neutral redox-probe FcMeOH solution (C) using a bare ITO electrode and ITO electrodes covered with the control CTAB-templated silica thin film, before (“non-extracted”) and after 20 min of extraction time (“extracted, 20 min”) as well as after additional 10 min of extraction (“extracted, 20+10 min”). The scanning rate was 20 mV/s.

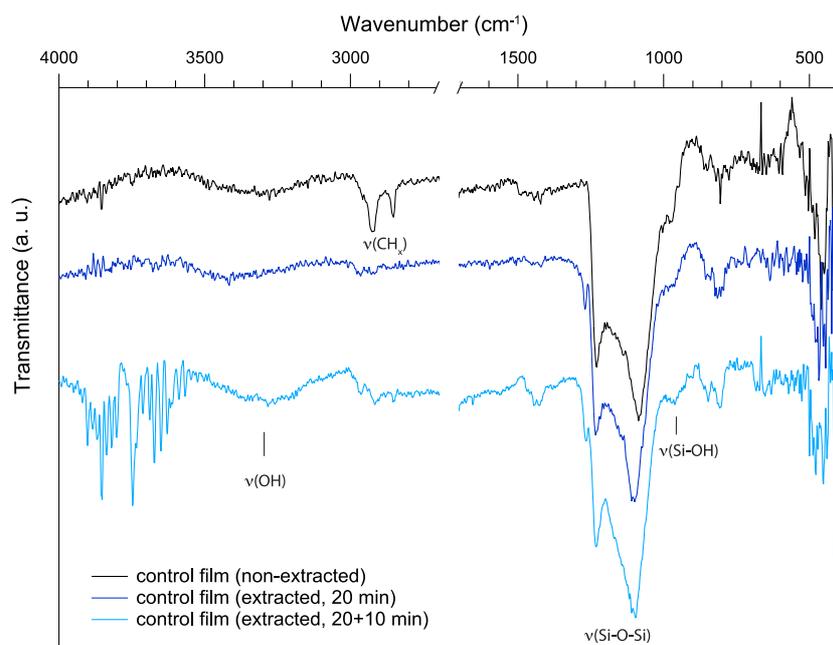


Figure S2. Infrared spectra of the control silica thin film collected before (“non-extracted”) and after placing it in the extraction solution for 20 min (“extracted, 20 min”) as well as after additional 10 min of extraction time (“extracted, 20+10 min”).

Properties of the film

The film used for the EIS measurements had been checked with CV, IR, and GISAXS. CV curves of positive and neutral redox probes were obtained only on the non-extracted film because the contact with electrochemically active compounds like the redox probes after extraction could influence the following EIS measurements even in trace amounts. Based on the CV curve presented in Figure S3, the non-extracted film shows good coverage of the electrode, blocking the pathway of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ probe to reach the ITO electrode as its CV curve shows no Faradic current peaks. At the same time, shifted redox peaks of the neutral probe FcMeOH appear, which is characteristic for when the probe passes through the pores of the silica film still containing CTAB and indicative for the pores running through the entire thickness of the film. The extraction of the templating CTAB was followed by IR spectroscopy. As can be seen in Figure S4, the area of the absorption peaks belonging to the stretching modes of the alkyl chain drastically decreases after extraction revealing a successful elimination of CTAB from the pores.

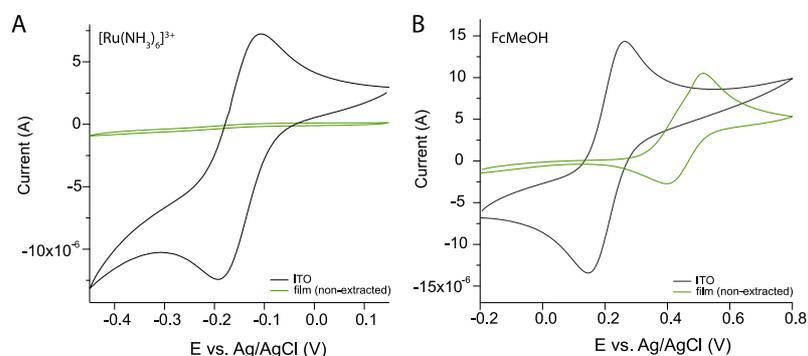


Figure S3. Cyclic voltammetric curves recorded with a positive redox-probe $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ solution (A) and a neutral redox-probe FcMeOH solution (B) using a bare ITO electrode and ITO electrodes covered with the control CTAB-templated silica thin film.

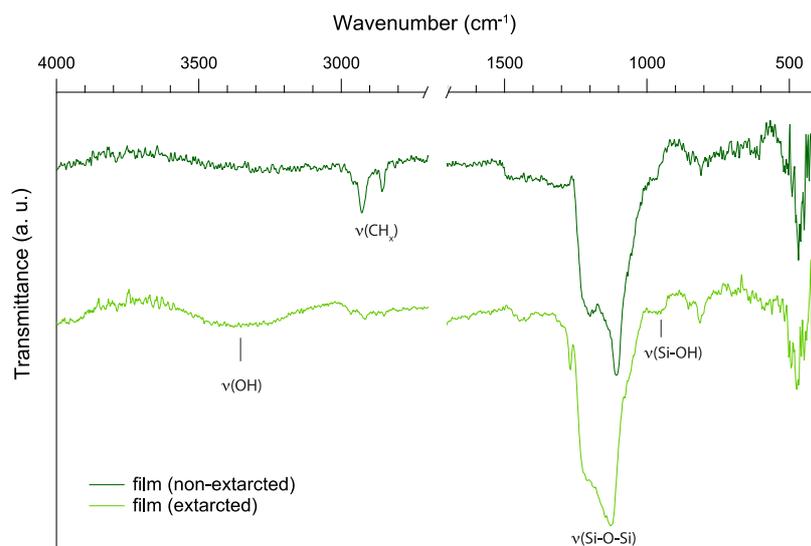


Figure S4. Infrared spectra of the silica thin film collected before (“non-extracted”) and after extraction (“extracted, 20 min”).

The GISAXS pattern of the film was obtained after 2 months from completion of the EIS measurements. A layer of the viscous ionic liquid remained on the top of the film as it could not be removed physically by for instance spinning or blowing pressurized nitrogen gas. Anyway, the 2 month-long-storage was useful to exclude the possible dissolution of the film in the ionic liquid. As shown in Figure S5, the film maintained its characteristic scattering peaks typical of the hexagonally ordered and vertically aligned channels (by rendering Miller indexes $q_1(10)$, $q_2(11)$, $q_3(20)$) and having a cell parameter of 4.29 nm, typical of mesoporous silica thin film deposited with EASA (Goux et al., *Chemistry of Materials*, 731–741, 2009). In addition, the ring-shape intensity appearing as peak q_4 in Figure S5B originates from the chain-chain nanosegregation of the ionic liquid with a correlation length of 1.7 nm (as also reported by Abdurrokhman et al. in ref (3)).

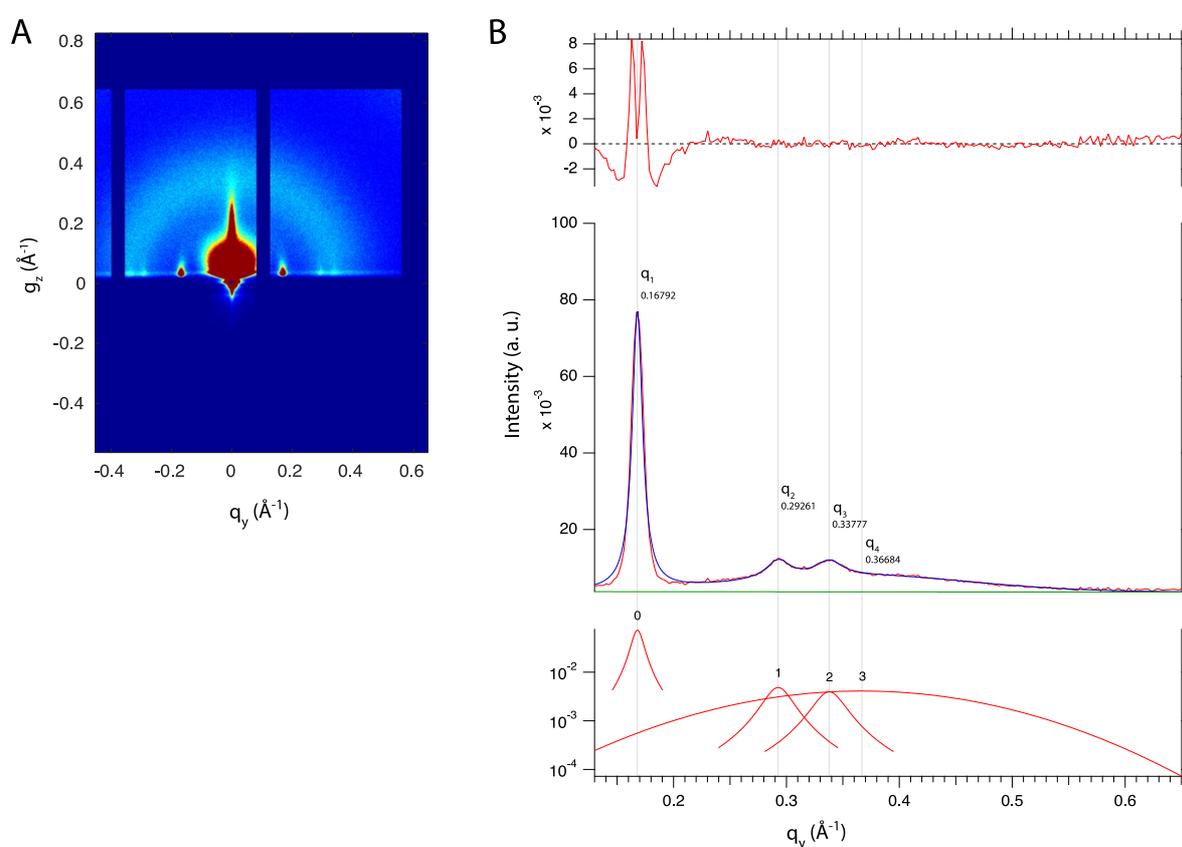


Figure S5. Grazing-incidence X-ray scattering (GISAXS) pattern of the silica thin film recorded 2 months after the EIS measurements, containing the ionic liquid $[\text{HC}_8\text{Im}][\text{TFSI}]$ inside its channels and partly on top of the film as a thin layer. A) 2D X-ray scattering pattern; B) X-ray scattering intensities integrated horizontally between $q_z = 0.01 \text{ \AA}^{-1}$ and $q_z = 0.05 \text{ \AA}^{-1}$ and analyzed by multi-peak fitting.

(3) Abdurrokhman, I., Elamin, K., Danyliv, O., Hasani, M., Swenson, J., and Martinelli, A.; Protic Ionic Liquids Based on the Alkyl-Imidazolium Cation: Effect of the Alkyl Chain Length on Structure and Dynamics, *J. Phys. Chem. B* 2019, 123, 4044–4054

Morphological properties of the film

The morphological properties of the mesoporous film, such as pore diameter and film thickness have been estimated, with the purpose of supporting the reader in understanding the double layer structure. These estimations are based on the extensive knowledge available in numerous publications on mesoporous silica thin films. Regarding the thickness, Goux et al. (Chemistry of Materials, 2009, 731–741) has revealed that the thickness of the CTAB-templated films synthesized with the EASA method has a linear dependency on deposition time. To estimate the thickness of the studied silica thin film (deposited for 25 s), two thickness values have been used: i) 83 nm after 30 s of deposition time as reported by Despas et al. (Journal of Solid State Electrochemistry, 2015, 19, 2075–2085) and ii) 50 nm at 20 s deposition time from the fitted curve (Figure 4C) reported by Goux et al. (Chemistry of Materials, 2009, 731–741). As the synthesis parameters of the film studied here by us were identical to the referenced publications, its thickness could be estimated to 65 nm. To avoid overestimation of the specific capacitance, the pore size of the silica thin film was estimated based on the highest reported pore size that was observed in a CTAB-templated, hexagonally ordered mesoporous silica thin film that has not been exposed to heat treatment of higher than 130 °C. Such hexagonally ordered mesoporous silica thin film, reported by Gibaud et al. (Europhysics Letters, 2003, 63, 833–839), has also been synthesized from a 50:50 EtOH:H₂O solution and showed an hexagonal lattice parameter of 4.78 nm (very close to 4.29 nm measured for the studied film) along with a pore size of 3.5 nm. Finally, from geometrical considerations and by knowing the pore size (3.5 nm in diameter) and the lattice parameter of the unit cell of the hexagonal structure (4.3 nm), one can estimate a porosity of 0.57 (i.e. 57% of the electrode's surface is not covered by silica).

Open circuit potentials measured before the EIS

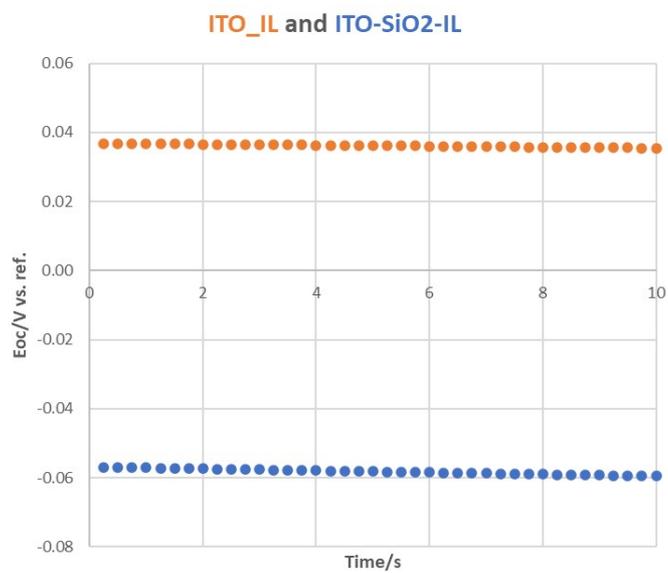


Figure S6. The open circuit voltage measured prior to the EIS measurements for the bare ITO surface and the ITO surface covered by a thin film of mesoporous silica.

II. Additional data obtained by BDS

The frequency dependence of the phase angle, $\phi(\nu)$, also mentioned in the main text of the manuscript, is shown below in Fig. S6a. The real part of permittivity, $\epsilon'(\nu)$, is shown in Fig. S6b and reveals a strong frequency (ν) dependence. Towards the lowest frequencies, $\epsilon'(\nu)$ increases rapidly and deviates from the expected stable plateau. This shape of $\epsilon'(\nu)$ at low frequencies, which is typical of ionic conductors but has also been observed in many ionic liquids, has been discussed to arise from strong electrode polarization effects [ref (4)]. These effects are observed when ion conducting materials are investigated with impedance and dielectric spectroscopy and arise from the accumulation of charges at the electrode forming thin layers that act as blocking electrodes. Unfortunately, these electrode polarization effects hamper the determination of the intrinsic dielectric properties but are at the same time important for the design of technological devices like fuel cells or double layer capacitors. Different modelling approaches based on equivalent electrical circuits can be used to account for these phenomena of electrode polarization, as thoroughly discussed in the work by Emmert et al. [ref (4)]. For the protic ionic liquid $[\text{HC}_8\text{Im}][\text{TFSI}]$ investigated in this work, $\epsilon'(\nu)$ takes values higher than 10^7 when the frequency is below 1 Hz at room or higher temperatures; a giant value that is, however, not unusual for ionic liquids, including those based on imidazolium cations [ref (4)]. For temperatures lower than 253 K, this upward trend of $\epsilon'(\nu)$ is not evidenced due to the overall shift of the curves towards lower frequencies, thus falling outside the window covered by the broadband spectrometer.

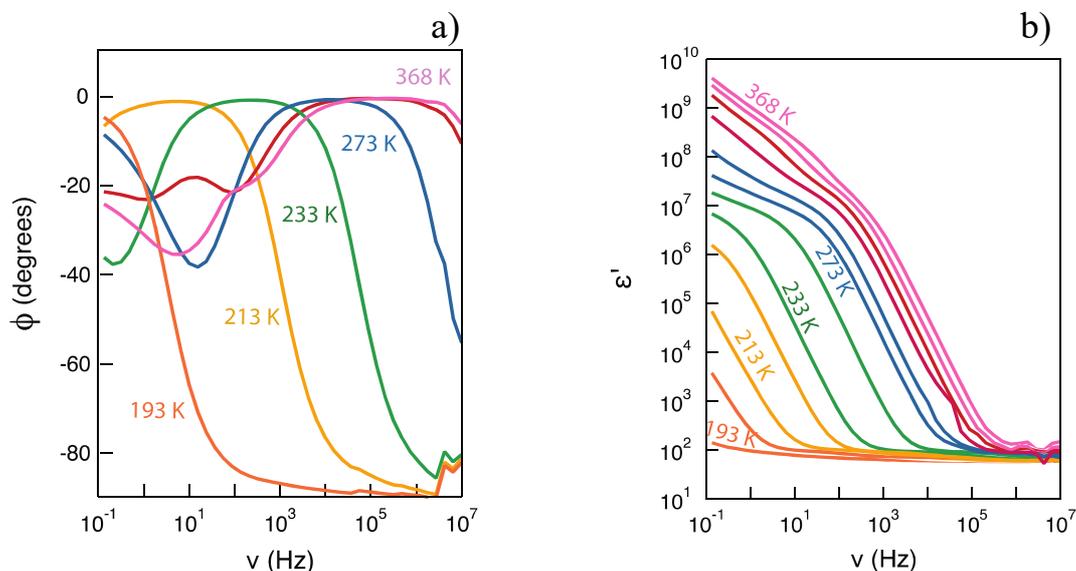


Figure S7. Frequency dependence of the phase angle (a) and of the real part of permittivity (b) for selected temperatures.

(4) S. Emmert, M. Wolf, R. Gulich, S. Krohns, S. Kastner, P. Lunkenheimer and A. Loidl, *European Physical Journal B*, 2011, **83**, 157–165

III. EIS measurements obtained in the three- or two-electrode cell

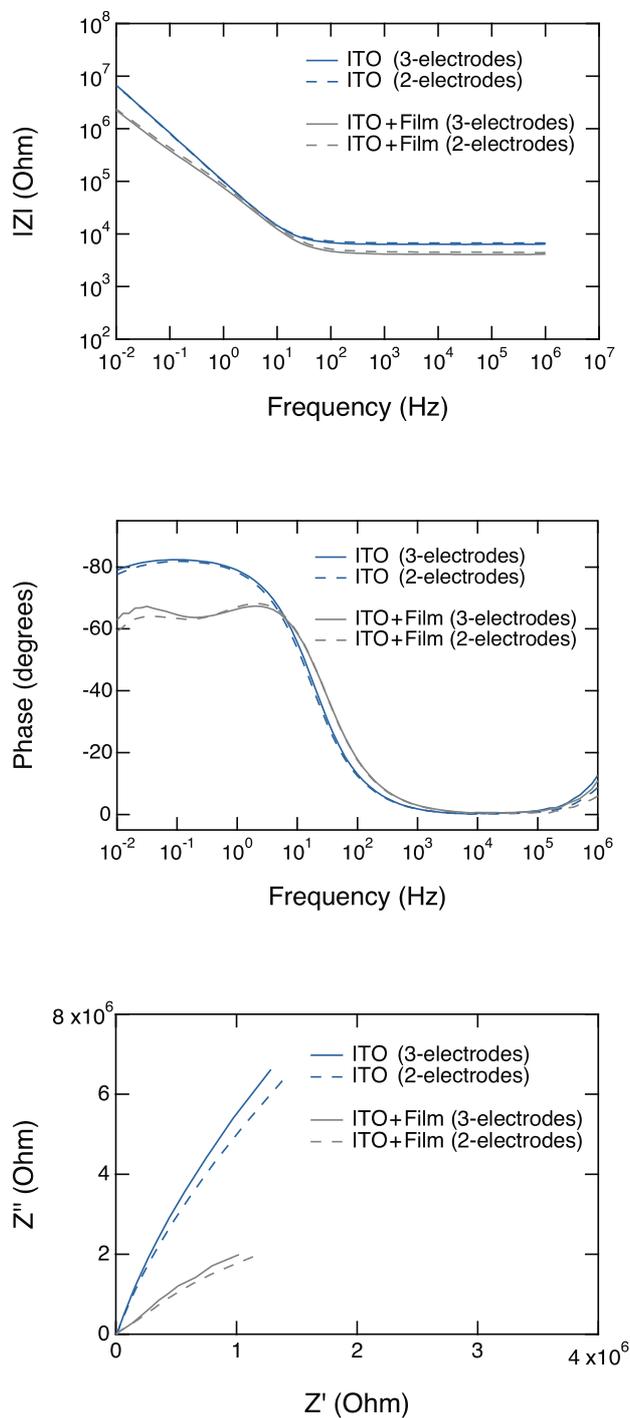
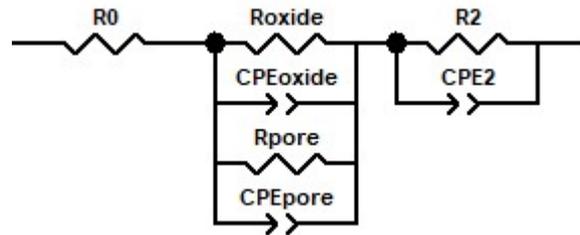


Figure S8. Comparison of results obtained by using a three- or a two-electrodes cell showing the modulus of Z (top panel), the phase angle (mid panel) and the Z'' as a function of Z' (bottom panel).

IV. Modelling equivalent circuit



R_0	R_{oxide}	CPE oxide	R_{pore}	CPE pore	R_2	CPE_{dl}
$k\Omega$	$k\Omega$	αF	$k\Omega$	αF	$k\Omega$	αF
4.51	7.50e6	4.60E-3	95.43	5.55	8.28e3	3.97

Figure S9. Equivalent circuit used for modelling the impedance spectra of the $HC_8Im][TFSI]/ITO+Film$ cell and estimate electrochemical parameters.

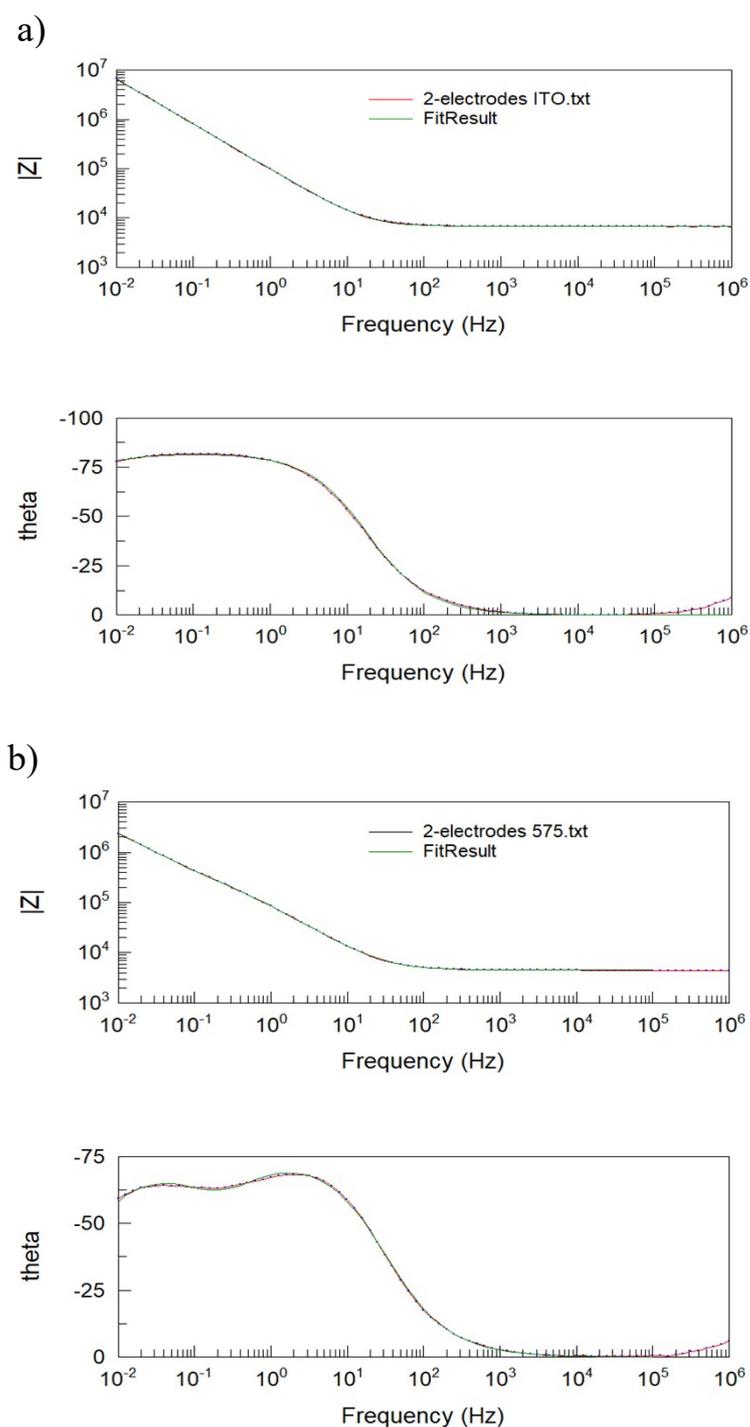


Figure S10. Plots of the frequency dependent modulus of impedance (top) and phase angle (bottom) comparing the experimentally recorded data (dots) with the curves obtained by the fitting model (solid lines). The two cases of the bare ITO surface and the ITO surface covered by a thin film of mesoporous silica are shown in a) and b), respectively. The χ^2 value of the fit was 0.02 for the case of ITO (a) and 0.0007 for the case of ITO-Film (b).

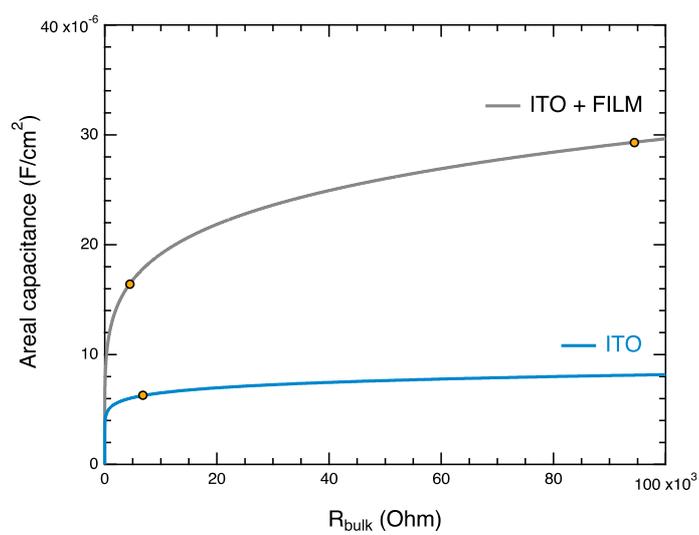


Figure S11. Areal capacitance simulated for varying values of R_{bulk} using the expression given in Eq. (1) reported in the main manuscript.