Supplementary Material (ESI) for Chemical Communications

Supplementary information:

High-Ion Conducting Solidified Hybrid Electrolytes by Self-Assembly of Ionic Liquids and TiO_2

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Fig. S1 The TiO_2 electrolytes with different compositions, and their phases and activation energy values (Ea).

phase	IL/Ti	$TiCl_4$	BMI TFSI	MeOH	formic acid	Ea(eV)
solid	0	1	0	2.8	3.1	
	0.1	1	0.1	2.8	3.1	
	0.2	1	0.2	2.8	3.1	0.25
quasi-solid	0.25	1	0.25	2.8	3.1	0.27
	0.3	1	0.3	2.8	3.1	0.25
	0.35	1	0.35	2.8	3.1	0.23
	0.4	1	0.4	2.8	3.1	0.25
	0.45	1	0.45	2.8	3.1	0.23
	0.5	1	0.5	2.8	3.1	0.23
liquid-like	0.6	1	0.6	2.8	3.1	0.25
	0.8	1	0.8	2.8	3.1	0.23
	1.2	1	1.2	2.8	3.1	0.21
	1.6	1	1.6	2.8	3.1	0.23

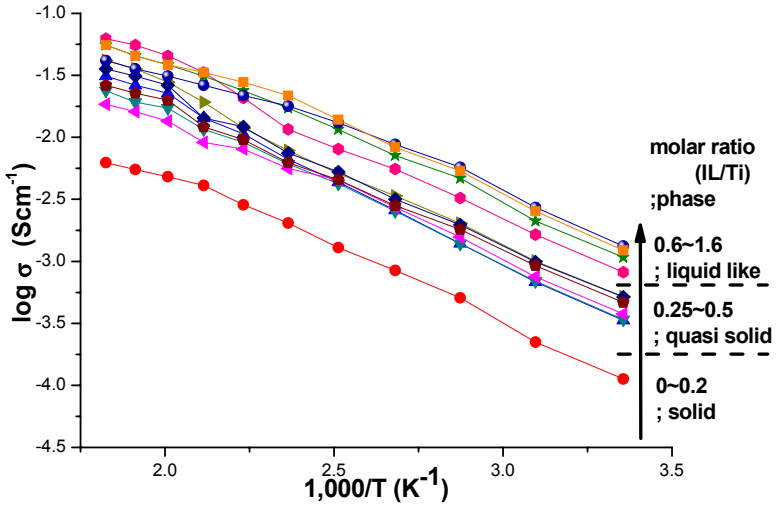

Fig. S2 Arrhenius plots of TiO_2 electrolytes with different molar ratio of the BMI TFSI and TiO_2 (IL/Ti). The Arrhenius plots log σ vs 1000/T also show the step increase with phase transition of the TiO_2 electrolytes in temperature region of 25 ~ 200°C. The linear polts let to estimated activation energies within the range 0.21 ~ 0.27 eV between 25 ~ 275 °C. (see also Table S1)

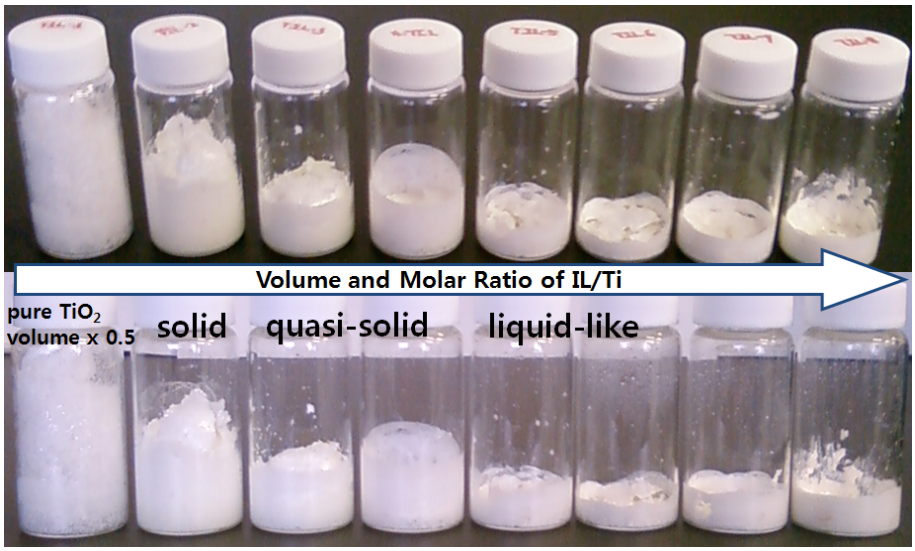

Fig. S3 Photographs of the TiO_2 electrolytes in vials. The product volumes were decreased by increasing the ionic liquid. These illustrate a macroscopic shrinkage of the samples, and reveal an influence of ionic liquid in the self-assembly process.[23-24] Probably, volume change can be driven by interactions between of ionic liquid and TiO_2 matrix.

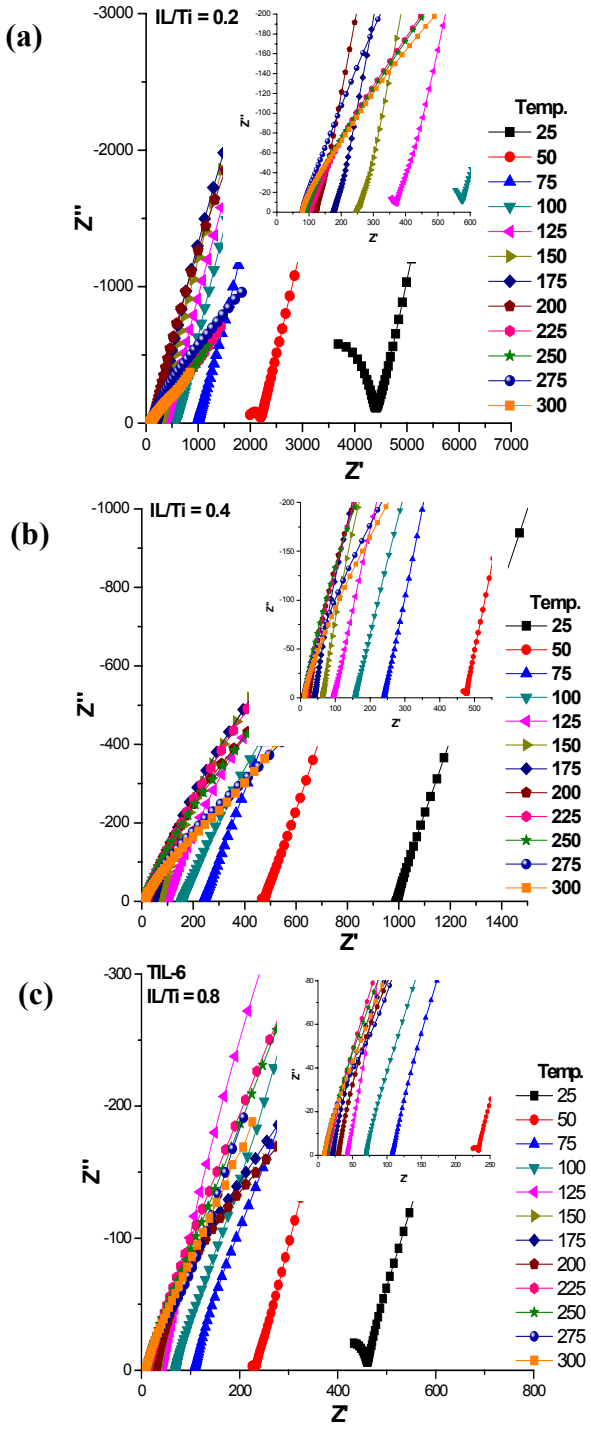

Fig. S4 Selected impedance spectra obtained in various temperature of TiO_2 electrolyte with different molar ratio of (a) IL/Ti = 0.2; solid, (b) IL/Ti = 0.4; quasi-solid and (c) IL/Ti = 0.8; liquid-like phase. The insets present the spectra on high-frequency, respectively.

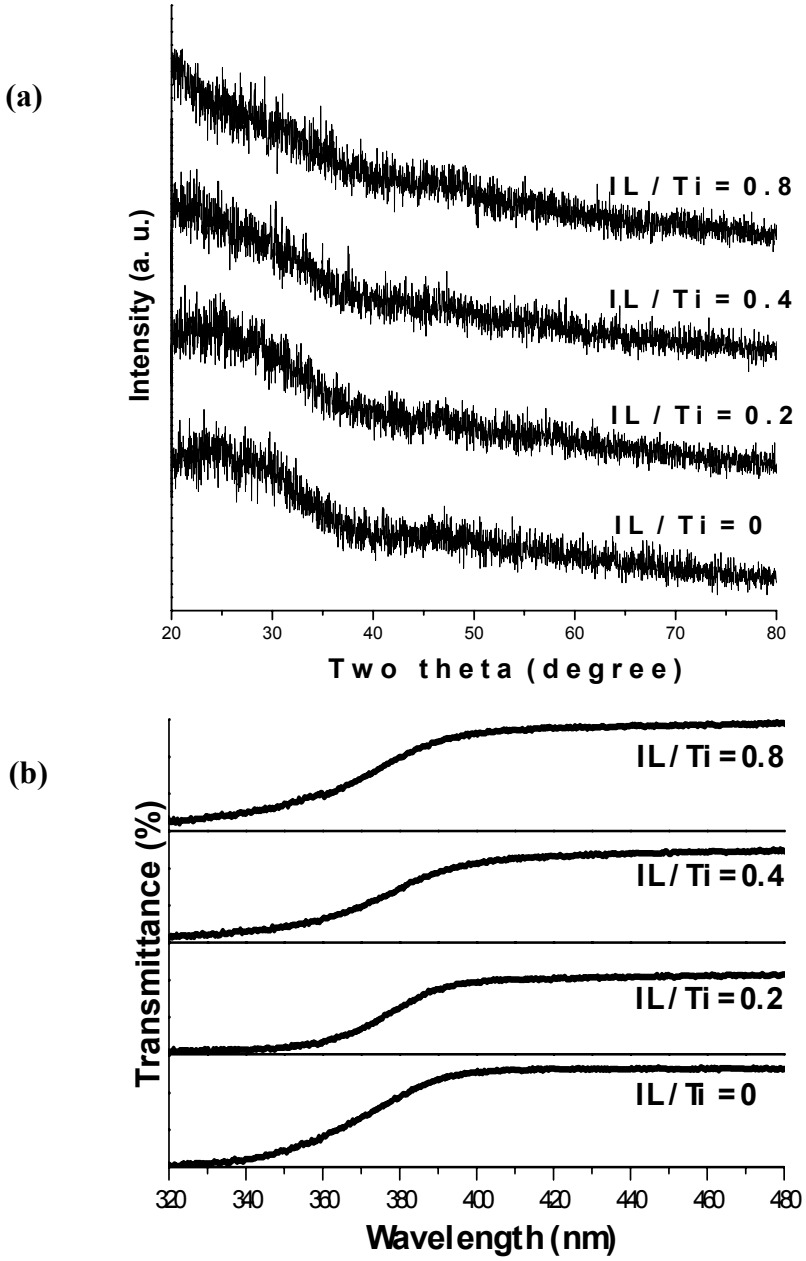

Fig. S5 Selected (a) X-ray diffraction patterns and (b) Transmittance UV-Vis spectra of the TiO_2 electrolytes with different molar ratios of IL/Ti = 0; amorphous TiO_2, IL/Ti = 0.2; solid, IL/Ti = 0.4; quasi-solid and IL/Ti = 0.8; liquid-like phase, respectively. The results of pure TiO_2 (IL/Ti = 0) are also showed. In the UV-Vis result, clearly the electrolyte samples present characteristic bands of TiO_2 at ~320 nm. The X-ray diffraction patterns, the oxides are formed mainly with the amorphous structure.

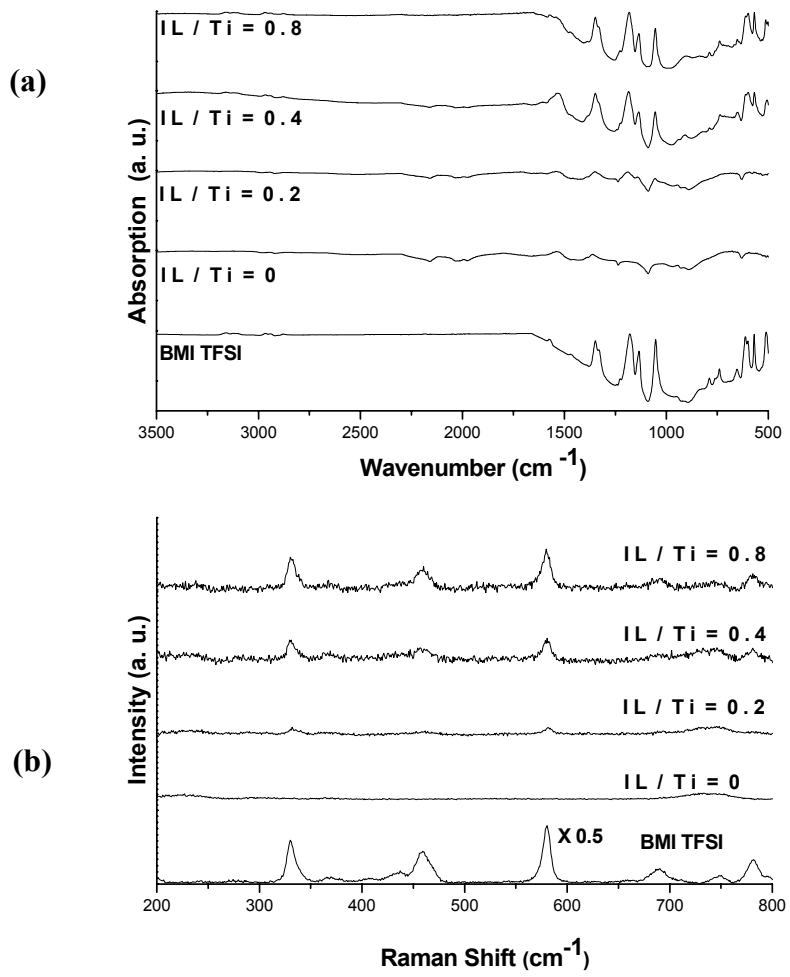

Fig. S6 Selected (a) FT-IR and (b) Raman spectra (with the 632.8 nm laser) of the TiO_2 electrolytes with different molar ratios of BMI TFSI, IL/Ti = 0; ionic liquid (BMI TFSI), amorphous TiO_2, IL/Ti = 0.2; solid, IL/Ti = 0.4; quasi-solid and IL/Ti = 0.8; liquid-like phase, respectively. All the samples spectra are very similar and are in agreement with the previously described spectra of pure ionic liquid. These results indicate that the increase of the ionic liquid amount in the matrix.