

Supporting Information

Unveiling the Relationship between the Surface Chemistry of Nanoparticles and Ion Transport Properties of the Resulting Composite Electrolytes

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Experimental

Surface modification of silica nanoparticles.

The surface modified silica nanoparticles are synthesized as shown in Scheme 1. For step 1, the aerosol 300 silica (A300) nanoparticles was firstly treated with hydrochloric acid for 1 h followed by washing and drying to hydroxylate their surfaces. Then in step 2, the aminophenyl group-functionalized silica nanoparticles (AP-SiO₂), amide group-functionalized silica nanoparticles (AM-SiO₂) and mercapto group-functionalized silica nanoparticles were achieved by refluxing the hydroxylated silica with p-aminophenyl triethoxysilane, 3-urea triethoxysilane and (3-mercaptopropyl)triethoxysilane, respectively, in toluene for 48 h under nitrogen. To obtain the sulfonate group-functionalized silica nanoparticles (SU-SiO₂), the as-prepared mercapto group-functionalized silica nanoparticles were treated with H₂O₂ (33 vol%) and then acidification with 0.05 M sulfuric acid.

Preparation of ionic liquid-based electrolytes.

The ionic liquid electrolyte was prepared by first mixing guanidinium thiocyanate (GNCS) and N-methylbenzimidazole (NMBI) and melting under 90 °C for 1 h. Then the 1-allyl-3-methylimidazolium iodide (AMII), 1-hexyl-3-methylimidazolium iodide (HMII) and iodine (I₂) were added to the above solution. The molar ratio of GNCS/NMBI/AMII/HMII/I₂ is 1.2/1.2/8/8/1. To prepare composite electrolytes, the AP-SiO₂, AM-SiO₂ or SU-SiO₂ nanoparticles with different weight ratios were blended with the ionic liquid electrolytes separately.

Measurements.

Transmission electron microscope (TEM, HT7700) was investigated to observe the morphology of nanoparticles. Fourier infrared spectroscopy (FTIR) and Zeta potential analysis of nanoparticles was measured using the TENSOR-27 spectrophotometer (Bruker Co.) and Zetasizer NANO ZS ZEN3600 (Malvern Instruments Ltd.). The nanoparticles were firstly dispersed in deionized water and then sonicated for 30 min to test the stable Zeta potential. The average values were obtained by 6 parallel tests. The ionic conductivity of electrolyte was carried out on the symmetrical stainless steel/electrolyte/stainless steel cells by electrochemical impedance spectroscopy (EIS) measurement, which was performed on the Solartron 1255B/1287 system at frequency range from 0.1 to 10^6 Hz with amplitudes of 10 mV. The conductivity (σ) was calculated from the ionic series resistance (R_s) according to the equation of $\sigma = l/(R_s S)$, where l and S are the thickness and area of active electrolyte, respectively. The apparent diffusion coefficient of ions (D_{app}) was tested by linear sweep voltammetry (LSV) on the symmetrical Pt/electrolyte/Pt cells at a scan rate of 5 mV s^{-1} and calculated from the limiting current density (J_{lim}) by the following equation $D_{app} = J_{lim} l / (2nCF)$, in which l is the thickness of electrolyte, n is the number of electrons in the redox reaction, C is the bulk concentration of ion species and F is the Faraday constant. The fluorescence microscopy images were taken from an inverted fluorescence confocal scanning laser microscope (FCLM, Nikon Ti-U) by exciting the samples with a mercury lamp.

Supplementary Figures

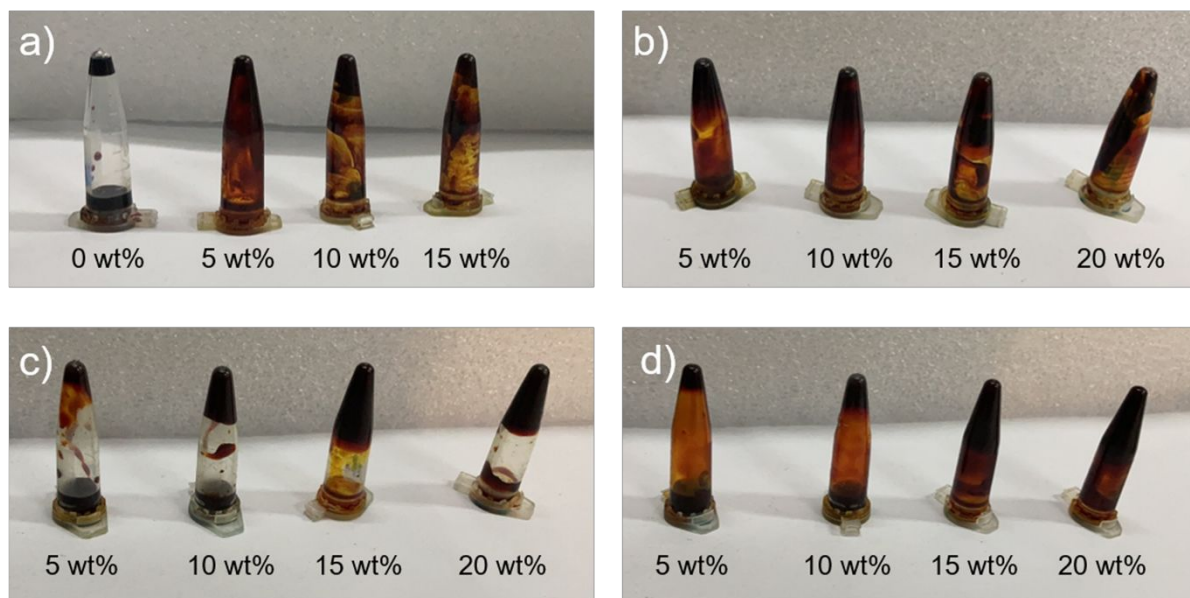


Figure S1. The bottom-up photographs of the electrolytes with different nanoparticles: (a) SiO₂, (b) AP-SiO₂, (c) AM-SiO₂ and (d) SU-SiO₂.

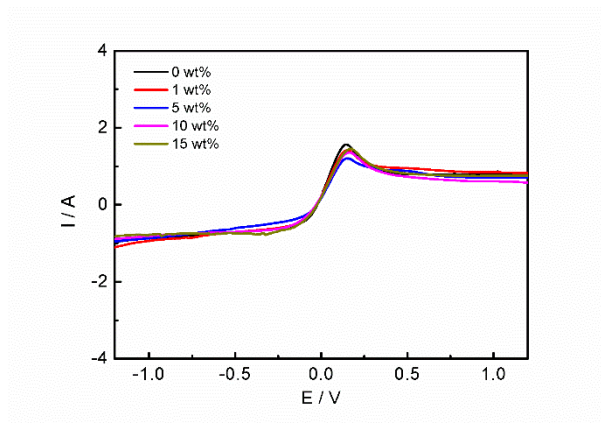


Figure S2. Linear sweep voltammograms (LSV) of electrolytes with different amount SiO₂.

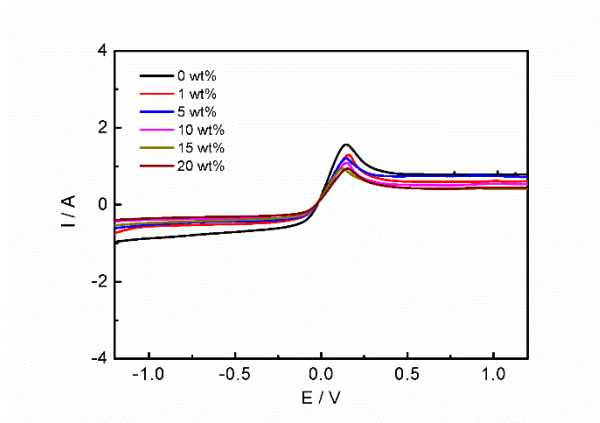


Figure S3. Linear sweep voltammograms (LSV) of electrolytes with different amount AP-SiO₂.

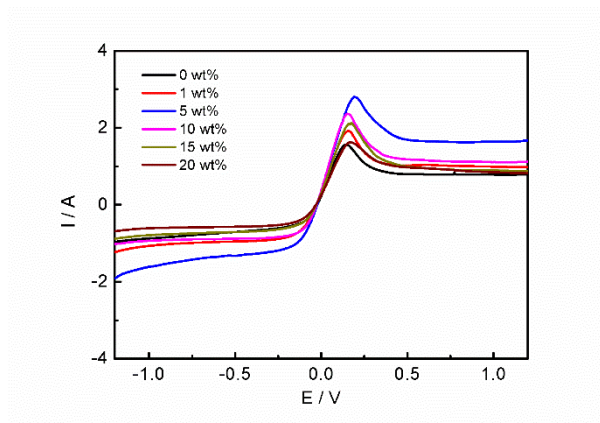


Figure S4. Linear sweep voltammograms (LSV) of electrolytes with different amount AM-SiO₂.

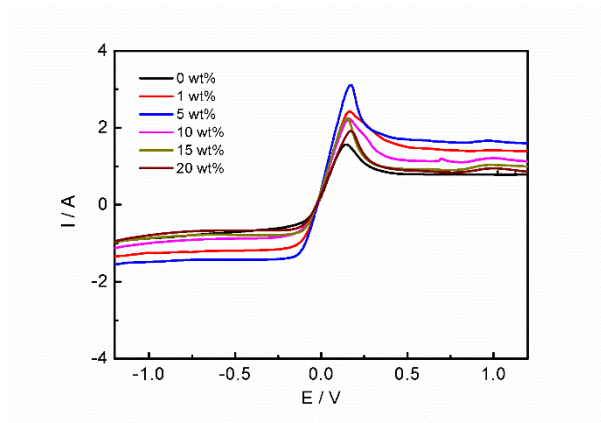


Figure S5. Linear sweep voltammograms (LSV) of electrolytes with different amount SU-SiO₂.