Biopolymer based nanocomposite ionogels: high performance, sustainable and solid electrolytes

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Supporting information

Materials

Silanized hydroxypropyl methylcellulose (Si-HPMC) as well as silica nanofibers (NFs) were prepared as described elsewhere[1,2]. 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES, ≥ 99.5 %) was provided by Sigma Aldrich (Germany) and acetonitrile was obtained from Carlo Erba (France). 1,3-dimethylimidazolium methylphosphonate (MMIm MePhos, >98%) and N-propyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr13 TFSI, 99%) were purchased from Solvionic (France) and were used as received. All the other reagents used were of AR grade.

Hydrogel synthesis

Si-HPMC polymer was dissolved in 0.2 M NaOH aqueous solution (30.9 mg ml^{-1}, pH > 12.5), then two dialyses with the molecular weight cut off of 6-8 kDa were performed in 0.09 M $NaOH_{aq}$. The acidic buffer solution (BS) at pH 3.2 was prepared by mixing 6.2 g of HEPES, 1.8 g of NaCl and 60 ml of 0.1 M HCl aqueous solution. The volume was adjusted to 100 ml with distilled water. The hydrogel precursor solution was then obtained by mixing 1 volume of the above Si-HPMC basic solution contained in one luer-lock syringe with 0.5 volume of acidic BS in another luer-lock syringe, by interconnection of both syringes; the final pH is 7.4. This mixture was injected into a teflon mould and the gel point was reached after 30-40 min. To ensure the complete gelification the samples were kept enclosed at humid atmosphere at room temperature for 2 weeks. The 2-week aged hydrogels were taken out of moulds and their diameters and heights were measured with a micrometer. To prepare Si-HPMC-NFs hydrogels we previously dispersed the desired amount of NFs into the buffer solution (NFs/BS) using an ultrasonic bath for 2h. The nanofibers amount inside each hydrogel is given as weight percentage of NFs with respect to the mass of pure Si-HPMC hydrogel

[1] Bourges, X.; Weiss, P.; Daculsi, G.; Legeay, G. *Adv. Colloid Interface Sci.* **2002**, *99*, 215-228.
[2] Rambaud, F.; Vallé, K.; Thibaud, S.; Julián-López, B.; Sanchez, C. *Adv. Funct. Mater.* **2009**, *19*, 2896-2905.

(without nanofibers). A pure hydrogel consists of 98 wt% of water and 2 wt% of Si-HPMC polymer.

Si-HPMC ionogel preparation

The 2-week old Si-HPMC and Si-HPMC-NFs hydrogels were put into 2 successive baths of MMIm MePhos ionic liquid during 24h to exchange the aqueous solution against the ionic liquid. After drying in an oven (24h at 50 °C) the ionogels containing ionic liquid were placed for 24h into soxhlet to exchange the MMIm MePhos against acetonitrile. At the end the samples were immediately put into 2 successive baths of Pyr13 TFSI ionic liquid during 24h following by 24h-drying at 50 °C in an oven. After each step the sample was weighted and to evaluate the amount of solvent into Si-HPMC matrix. The dimensions of the sample were also measured after each step using a calliper.

Instrumentation

Fourier-transform infrared spectroscopy (FTIR) was performed on Bruker Vertex70 spectrometer in the attenuated total reflection mode (ATR). The spectra resulted from averages of 100 scans at 4 cm^{-1} resolution, between 500 and 2500 cm^{-1}.

Thermogravimetric analysis (TGA) were carried out on SETARAM TGA 92 - 16.18 from room temperature up to 600 °C with heating rate of 5 °C/min and under air. Each sample was vacuum dried at 50 °C during 24h before analysis.

Impedance spectroscopy. The ionic conductivities of our Si-HPMC and Si-HPMC-NFs ionogels were determined by the complex impedance method at 25 °C, using a BioLogic VMP2-Multichanel Potentiostat. The frequency range used for impedance measurements was 185 kHz to 20 mHz and the amplitude used was 7mV. All the samples were vacuum dried at 50 °C during 24 h prior to measurement. Residual water was evaluated by TGA (Fig. 3) to be less than 700 ppm.

Scanning electron microscopy (SEM) was done on JEOL 7600-F microscope at 5kV accelerating voltage. The samples were metalized prior to their observation.

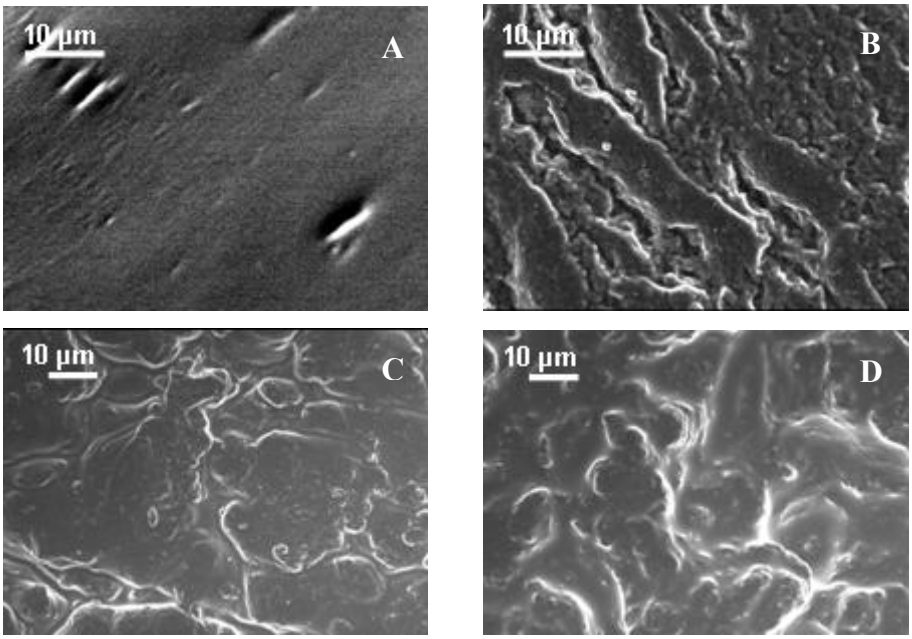

Figure S1. SEM images of: Si-HPMC ionogel containing MMIm MePhos (A); Si-HPMC ionogel containing Pyr13 TFSI (B); Si-HPMC-1 wt% NFs ionogel with Pyr13 TFSI (C); and Si-HPMC- 4 wt% NFs ionogel (D) with Pyr13 TFSI.