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ARTICLE TYPE

Highly efficient solid polymer electrolytes using ion containing polymer microgels†

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A solid polymer electrolyte exhibiting high ionic conductivity (reaching ca. $10^{-4.8}$ S/cm at 25 °C) is fabricated by using ion containing polymer microgels of lithium tris(perfluorophenyl) (2,3,5,6-tetrafluoro-4-(2-(2-(vinyloxy)ethoxy)ethoxy)phenyl) borate. This solid polymer electrolyte shows great possibilities for use in large-capacity lithium ion batteries.

Ion containing polymers are receiving increased attention due to their potential use in batteries, fuel/solar cells, supercapacitors, and actuators.[1] Of particular interest are chains where a fraction of segments are negative charged and the counter cation is mobile under an electric field.[2] Since the cation is the only conducting ion, the materials made by those ion containing polymers are also called "single-ion conductors". Such conductive materials can offer two main advantages over the traditional materials of salt-in-polymer mixtures: unity transference number, and the absence of detrimental anion polarization.[3] These merits can allow a high power density and recharging rates achievable in the solvent-free energy conversion/storage devices. However, the conductivity of these conductive materials as solid polymer electrolytes are low, precluding their use in practical applications. Exploring novel approaches to promote the conductivity of these materials is one of the keys for future development in this area.

In order to improve the conductivity, two strategies are widely employed: i) designing new anionic moieties whose negative charges can delocalize to minimize ion pairing with the cations and thus favor the creation of a charged species for conduction; ii) using polymers of flexible backbones, so as to promote the transport of the charged species.[1-3] In both of the two approaches, however, the conductivities of the conductive materials fabricated directly with those ion containing polymers are still of order of 10^{-5} S/cm at 25 °C, 10 times lower than the minimum practical requirement.[4] A generally acceptable explanation is that the dipole−dipole interactions between the ion pairs along polymer chains may cause clustering of ion-rich moieties (which in effect physically cross-link polymer chains) within a nonpolar matrix; in such cases, one expects a large activation barrier for inter-cluster hopping.[5] In this respect, from a structural point of view, fabricating the conductive materials via manipulating the micro-/nanostructures of the ion containing polymers is desirable for promoting the conductivity, and have therefore recently attracted a great deal of attention.[6] The underlying idea of this approach is to facilitate ion transport along phase-separated ionic domains in a structural matrix. The confinement provided by nanoscale ionic channels is thought to be an important factor that enhances the ion transport rate by offering short ion conduction pathways. To date, a significant effort has been aimed at developing conductive materials by using linear, graft, or star copolymers that have the ability to produce unique micro-/nanostructures, which typically involves self-assembly of polymer chains under well-controlled conditions.[6] Despite the exciting progresses, the challenge of fabricating the conductive materials with micro-/nanostructures of ion containing polymers still remains.

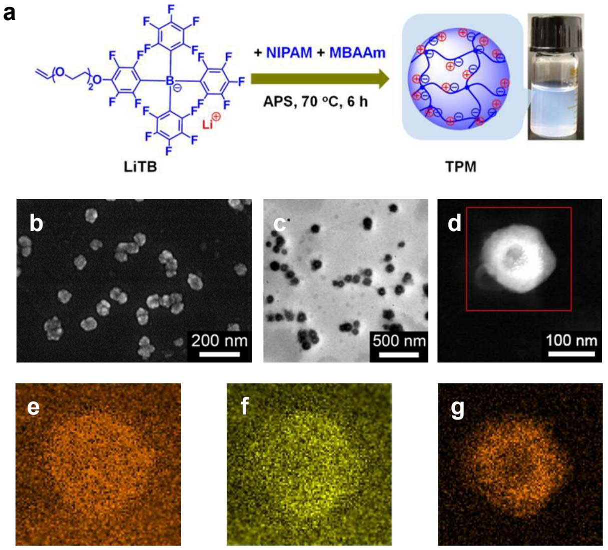

Fig. 1 (a) Illustration of the synthesis of TPM. Typical (b) SEM and (c,d) TEM images, (e) EDX carbon, (f) nitrogen and (g) fluorin maps based on the selected area shown in (d), of the TPM.

Herein, we propose a novel approach (Fig. 1a; see ESI† for the detailed procedures) to fabricate the conductive materials of ion

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containing polymers, starting from one-pot aqueous synthesis of ion containing polymer microgels (we denote these microgels as TPM). Polymer microgels are colloids of three-dimensional crosslinked polymer gel network structure internally, which make the microgels readily combine the characteristics of both colloids and polymers.[7] Polymer microgels may offer several advantages over other polymer systems to fabricate the conductive materials: simple synthesis, easy functionalization, uniform size distribution, and tunable dimension. Moreover, in comparison with the linear, graft, or star copolymers reported in previous arts, the polymer chains between the crosslinking points on the polymer microgels might exhibit a relatively slow motion,[8] which is favorable for preventing clustering of ion-rich moieties.[2,6] These ion containing polymer microgels should present the prospects for fabricating conductive materials of efficient lithium-cation Li^+ conductivity.

We commence our study by the synthesis of the TPM by free radical copolymerization of lithium tris(perfluorophenyl)(2,3,5,6-tetrafluoro-4-(2-(2-(vinyloxy)ethoxy)ethoxy)phenyl)borate (LiTB; see Fig. S1, S2 and S3 in ESI† for ^1H, ^{13}C and ^{11}B NMR spectra, respectively; 8.2×10^{-3} mol L^{-1}), *N*-isopropylacrylamide (NIPAM; 8.5×10^{-2} mol L^{-1}), and *N*,*N′*-methylenebisacrylamide (MBAAm; 3.5×10^{-3} mol L^{-1}) using ammonium persulfate (APS; 3.4×10^{-3} mol L^{-1}) as an initiator at 70.0 °C. At the end of polymerization, the light-blue color (owing to the Tyndall effect) was observed in the dispersion (Fig. 1a). IR analysis (Fig. S4 in ESI†) confirmed the incorporation of LiTB moiety into poly(NIPAM) gel networks, as revealed by the characteristic band of C–O–C vibration at 1087 cm^{-1} of LiTB moiety, as well as the two typical bands of C–H vibrations of $–CH(CH_3)_2$ at 1385 cm^{-1} and 1367 cm^{-1} of NIPAM moiety. The weight percentage of lithium was determined to be ca. 3 wt% by thermogravimetric analysis (Fig. S5 in ESI†) combined with inductively coupled plasma-atomic emission spectroscopy analysis. Li 1s X-ray photoelectron spectra (Fig. S6 in ESI†) of the TPM exhibited a symmetrical peak, which has the typical binding energy as the lithium-cation Li^+ (E_b (Li 1s) = 55.8 eV).[9] Fig. 1b,c,d show SEM and TEM images of the TPM, indicating the formation of sphere-like morphology. Fig. 1e,f,g show energy dispersive X-ray (EDX) maps for carbon, nitrogen and fluorin, respectively, based on the area shown in the annular dark field (ADF) image (Fig. 1d). The edge of carbon and nitrogen EDX maps matches the result shown in ADF image, indicating that carbon and nitrogen are homogeneously distributed throughout the microgels; in contrast, fluorin is highlighted as a coronet-like distribution, suggesting that LiTB moiety might predominantly, but homogeneously, distributed on the surface of the microgels at a light penetration depth. Because the K edge of lithium is not detectable by EDX, the distribution of lithium was confirmed by using electron energy loss spectroscopy (EELS; see a line scan of normalized EELS intensities of carbon and lithium in Fig. S7 in ESI†). The observations support our hypothesis that the polymer microgels where Li^+ is mainly uniformly dispersed on the surface layer at a light penetration depth were obtained.

Next, the TPM was made to solvent-free bulky materials by concentrating, putting onto a die, heating (up to 60 °C, which is above the volume phase transition temperature of the TPM; see Fig. S8 in ESI†) and then cooling down slowly, freeze-drying, and finally pressing (300 MPa)(Fig. S9 in ESI†). Fig. 2a shows the small-angle X-ray scattering (SAXS) profile for the fabricated bulky materials. Two distinct broad peaks and a low-angle upturn are observed. It is inferred that the materials are amorphous, as revealed by the absence of sharp unit cell reflections; this is consistent with the absence of crystallization/melting peaks in differential scanning calorimetry (DSC) curve (Fig. S10 in ESI†). The peak at q = 14.1 nm^{-1} primarily arises from the amorphous carbon side chain scattering. The scattering peak at q = 5.3 nm^{-1} corresponds to a spacing $2\pi/q$ = 1.2 nm and is assigned to pendant-backbone correlations in the ion containing polymers. The low-angle upturn is indicative only of random, long-range heterogeneity. No peak was recorded in the range of q = 1–3 nm^{-1} (the most common average spacing $d_{cluster}$ of ion clusters reported in literatures is 5 nm, corresponding to q = 1.3 nm^{-1}), indicating that ion clustering is absent in the materials.[5]

It is known that boron has much lower electronegativity than oxygen, nitrogen, carbon, or sulfur; as a result, borate anions are more inclined to delocalize charge to minimize ion pairing with Li^+ and thus provide more mobile Li^+ for conducting.[1,2] *Ab initio* calculations indicated that the ion dissociation energy of $LiBPh_4$ is similar to that of $LiN(SO_2CF_3)_2$, and much lower than that of $LiClO_4$, which was attributed to the four phenyl rings around boron greatly delocalizing the negative charge; perfluorinating the four phenyl rings can further lower the ion association energy, leading to a promoted conductivity of $10^{-6.9}$ S/cm at 25 °C.[2g] By reducing the ion clustering for facile ion transport, it is expect that the conductivity should be significantly increased.[5] We thus measured the conductivity of the fabricated solvent-free bulky materials by using a standard four-electrode method. As shown in Fig. 2b, the conductivities were low (in the order of ca. 10^{-11} S/cm, a typical value of Li^+ single-ion polymer conductors) at temperatures below T_g (a broad range of 11–38 °C, owing to the polydisperse of the length of subchains between two crosslinking points inside the polymer microgels; Fig. S10 in ESI†)[7a] of LiTB-rich moieties,[2g] but showed a rapid increase at the elevated temperatures. The conductivity reached ca. $10^{-4.8}$ S/cm at 25 °C, and ca. $10^{-4.2}$ S/cm at 60 °C, which are superior results for a Li^+ single-ion polymer conductor. The ion transport number t^+ was ca. 0.9, slightly below the expected value of unity.

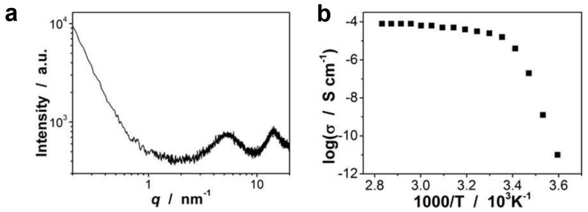

Fig. 2 (a) SAXS profile and (b) temperature-dependent conductivity for the solvent-free bulky materials fabricating by using the TPM.

Having demonstrated the feasibility of fabricating the material by using the TPM for Li^+ ion conduction, the electrochemical property of the TPM-material as a solid polymer electrolyte was characterized in a Li/TPM-material/stainless-steel cell by cyclic voltammetry. The measurement was performed at 60 °C between −0.2 and 5.0 V (vs. Li^+/Li) at a scanning rate of 1.0 mV s^{-1}. Clearly, Fig. 3a shows that the TPM-material as solid electrolyte was stable up to 5.0 V versus Li^+/Li. This important feature of the TPM-material might make it possible to consider the use of high-potential cathode materials that cannot be safely tested in liquid electrolytes owing to their lower electrochemical stability.[1e,6f]

To further demonstrate the feasibility of the TPM-material as a solid polymer electrolyte, a battery prototype based on the TPM-material was assembled using a lithium-metal negative electrode (anode) and a carbon-coated $LiFePO_4$ as a model active material for the positive electrode (cathode). As a proof of the concept, the formulation of the composite cathodes was 60 wt% $LiFePO_4$, 30 wt% TPM-material and 10 wt% carbon black, and the composite electrode was about 127 µm thick. Cycling tests were conducted at 60 °C and a rate of 0.1C, where C is the theoretical cathode capacity (170 mAh g^{-1} for $LiFePO_4$).[9] Fig. 3b shows the voltage profiles of the first cycle recorded for Li/TPM-material/$LiFePO_4$ prototype as a function of the capacity stored by the positive active material $LiFePO_4$. The capacity retention is ca. 156 mAh g^{-1}. The cycle-life of the prototype, which correspond to the returned capacity as a function of the cycle number, is shown in Fig. 3c. More than 90 cycles are observed without significant capacity-fading (the capacity retention is >90% of that recorded at the first cycle), revealing attractive performances compared with the literature results of lithium-metal batteries using linear, graft, or star copolymers as solid polymer electrolytes.[6]

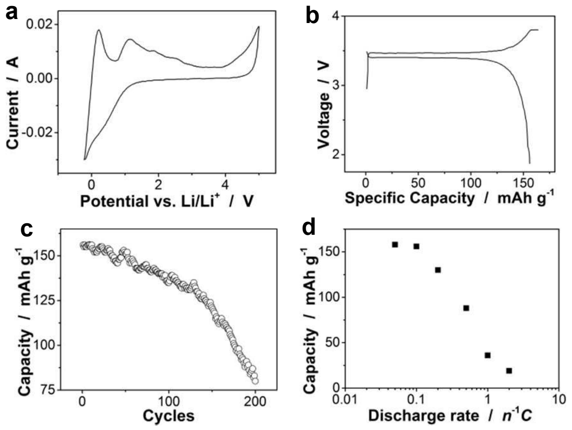

Fig. 3 (a) Cyclic voltammogram for a Li/TPM-material/stainless-steel cell. (b) The voltage profiles for the first cycle charging/discharging measured at a rate of 0.1C, (c) cycle-life measured at a rate of 0.1C, and (d) the discharged capacity as a function of the discharge rate, for a prototype Li/TPM-material/$LiFePO_4$. All measurements were conducted at 60 °C.

In addition, the power holding capacity of the battery prototype given by the discharged capacity as a function of the discharge rate is shown in Fig. 3d. As expected, when the discharge rate was increased, the cathode cannot sustain a high discharging current (fast Li^+ intercalation), and thus the capacity gradually faded.[10] The capacity decay may also due the react of the polymer electrolyte with lithium (Fig. S11 in ESI†), which becomes much significant after long cycles. Nevertheless, there is retention of more than 56% of the capacity at a 0.5C rate, indicating a good behaviour. In particular, the results at 60 °C are interesting as they hint at the possibility of a working temperature with comparable performances but 20 °C below the standard working temperature (80 °C) for state-of-art solid polymer electrolytes.[11]

In conclusion, we demonstrated the feasibility of fabricating conductive material by using ion containing polymer microgels, and its use as a solid polymer electrolyte, which could exhibit a considerable high conductivity and large electrochemical stability window. By using this ion containing polymer microgel based material as a solid polymer electrolyte and in the formulation of the composite cathode, we have been able to elaborate lithium-metal battery prototype with a considerable good gain in power performances. Our results underscore the vast potential of ion containing polymer microgels in developing future lithium-metal-based battery technology.

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