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ARTICLE TYPE

Metal organic framework-laden composite polymer electrolytes for efficient and durable all solid-state-lithium batteries

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Copper benzene dicarboxylate-metal organic framework (Cu-BDC MOF) was synthesized and successfully incorporated in a poly (ethylene oxide) (PEO) and lithium bis (trifluoromethanesulfonylimide) (LiTFSI) complex. The incorporation of Cu-BDC MOF has significantly enhanced the ionic conductivity, compatibility and thermal stability of the composite polymer electrolyte (CPE). An all solid-state-lithium cell composed of Li/CPE/$LiFePO_4$ was assembled and its cycling profile has been analyzed for different C-rates at 70 ˚C. The appreciable ionic conductivity, thermal stability and cycling ability qualify these membranes as electrolytes for all solid-state-lithium batteries for elevated temperature applications.

Introduction

The declining fossil fuel resources and global warming have alarmed the researcher's to identify alternative energy sources [1]. Although lithium-ion batteries remain as the mainstay for portable electronic devices such as laptop computers, mobile phones etc., their safety is limited due to the use of non-aqueous liquid electrolytes showing poor thermal stability, flammable reaction products and leakage of electrolyte and internal short-circuits [2]. These problems can be circumvented by replacing the non-aqueous liquid electrolytes by solid polymer electrolytes which possess several advantages such as high energy density, no-leakage of electrolytes, flame resistant and flexible geometry [3]. The development of polymer electrolytes have gone into two stages namely (i) dry solid polymer electrolyte and (ii) gel and composite polymer electrolytes. The use of dry solid polymer electrolyte composed of a polar polymer host and lithium salt is hampered by its poor ionic conductivity and rate capability at ambient temperature. The gel polymer electrolytes, on the other hand, exhibits appreciable ionic conductivity (order of 10^{-3} Scm^{-1} at 30 ^{o}C) and transport numbers. However, upon plasticization, they lose their mechanical integrity and leads to poor interfacial properties with lithium metal anode [4]. Recently, Zhu et al., intensively analyzed gel polymer electrolytes based on nonwoven fabric, glass fibre mats and a PVdF/Polyborate/PVdF- trilayer membranes which exhibited better mechanical strength, enhanced electrochemical properties, safety and low cost [5-7]. Xiao and co-workers introduced a novel environmental friendly and less expensive cellulose based gel polymer electrolytes for lithium-ion batteries and this type of gel polymer electrolytes offered higher lithium-ion transference number than the commercial separator [8]. Saito et al., [9] demonstrated a Lewis acid ionic groups-incorporated gel polymer electrolytes. The cycling performance of a calcium carbonate hard template-assisted three dimensionally macroporous polymer electrolytes was reported by Liu and co-workers recently [10]. Studies reveal that, composite polymer electrolytes can alone offer safe and reliable lithium batteries [11]. Generally, inorganic fillers (e.g. TiO_2, SiO_2, Al_2O_3) are widely incorporated in polymeric matrices in order to enhance the ionic conductivity and to improve thermal and mechanical properties. Substantially, it also improves the interfacial properties with lithium metal anodes. Numerous reports are available on the physical and electrochemical properties of composite polymer electrolytes for lithium batteries [12-16]. The metal organic frameworks (MOFs) which are micro porous solids comprising an infinite network of metal centres (or inorganic clusters) bridged by simple organic linkers through metal–ligand coordination bonds have attracted the attention of many researchers [17-19]. MOFs are widely used in catalysis, sensors, ion exchange, gas storage, purification, separation and sequestration and also widely employed to promote both electronic and proton conductivity [20]. Generally, incorporation of ceramic fillers grafted with organic groups has hybrid properties, which facilitate for better miscibility with PEO and thus promote ionic conductivity and mechanical integrity of the system [21]. The reports on MOF-laden composite polymer electrolytes for lithium battery applications are very scanty. In the present study, Cu-BDC MOF has been successfully synthesized by an electrochemical method and is suitably incorporated in a PEO+LiTFSI complex and its physical and electrochemical properties are described.

Experimental Procedure

The preparation and structural characterization analyses of synthesized Cu-BDC MOF have already been reported [22]. PEO (Aldrich, USA) and lithium bistrifluorosulfonylimide, LiTFSI (Merck, Germany), were dried under vacuum for 2 days at 50 and 100 ˚C, respectively. Cu-BDC MOF was also dried under vacuum at 50 ˚C for 5 days before use. Composite polymer electrolytes were prepared by dispersing appropriate amounts of Cu-BDC MOF in PEO - $LiN(CF_3SO_2)_2$ (as shown in Table 1) and hot-pressing into films as described elsewhere [23]. The composite electrolyte films had an average thickness of 30-50 μm. This procedure yielded homogeneous and mechanically strong membranes, which were dried under vacuum at 50 ˚C for 24 h for further characterization. The ionic conductivity of the membranes sandwiched between two stainless steel blocking electrodes (1 cm^2 diameter) was measured using an electrochemical impedance analyzer (IM6-Bio Analytical Systems) between the frequency ranges from 50 mHz and 100 kHz for various temperatures (0, 15, 30, 45, 60, and 70 ˚C). Symmetric non-blocking cells of the type Li/CPE/Li were assembled for compatibility, which was investigated by studying the time dependence of the impedance of the systems under open-circuit potential at 70 ˚C. The lithium transference number was calculated by the method proposed by Vincent and co-workers [24].

$$Li_t^+ = \frac{I_{ss}(V-I_0R_0)}{I_0(V-I_{ss}R_{ss})} \qquad \text{……………} \ (1)$$

DSC and TG-DTA measurements were performed in a N_2 atmosphere at a heating rate of 10 ˚C min^{-1} between the temperature ranges between -100 to +100 ˚C and 20 and 650 ˚C respectively.

The $LiFePO_4$/C cathode material was synthesized in the form of nanostructure powder through a mild hydrothermal procedure described by Meligrana et al.,[25]. The composite cathode was prepared in the form of a film (average thickness of about 70µm) by blending 10 wt.% of poly(vinylidene fluoride) as the binder (SolvaySolef 6020) with 20 wt.% of acetylene black (Shawinigan Black AB50, Chevron Corp., USA) as the electronic conductivity enhancer and 70 wt.% of $LiFePO_4$/C active material, thoroughly mixed in 1-methyl-2-pyrrolidone (Aldrich, USA). The slurry was coated onto an aluminum foil current collector. All preparations were performed in an argon-filled glove box (MBraunLabstar, Germany) having a humidity content below 1 ppm. The lithium metal was used as anode. The cycling of the cell was performed at 70 ˚C by an Arbin Instrument Testing System mode BT-2000, setting the cut off voltages to 2.50–4.00 V *vs*. Li/Li^+. The charge–discharge cycles were set at different current rates as reported earlier [25].

Results and Discussions

Thermal analyses

The DSC thermogram of the composite polymer electrolyte (sample S5 as this sample is found to be optimal in terms of ionic conductivity point of view) is illustrated in Figure 1.

The glass transition temperature of PEO+LiTFSI has been increased (towards positive side) from -54 to -50 ˚C upon addition of Cu-BDC MOF in the polymeric matrix. The increase in the value of 'T_g' has been attributed to (i) the effect of dispersed Cu-BDC MOF and (ii) confinement of the intercalated/exfoliated polymer chains within the filler galleries, that resists the segmental motion of the polymer chains and also indicates the plasticization effect that arises due to the mild retarding effect on the crystallization due to the added Cu-BDC MOF filler [26]. Figure 2 depicts the TG-DTA traces of sample S5 (75% PEO +10% Cu-BDC MOF + 15% LiTFSI).

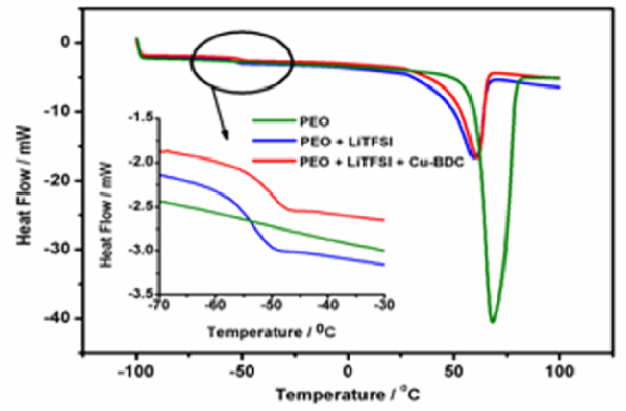

Figure 1. DSC traces of PEO, PEO+LiTFSI and PEO+LiTFSI+ Cu-BDC MOF.

Generally the heating process brings a lot of changes in the composite electrolytes, finally leaving behind inert residues. A weight loss of around 3% has been observed around 50 ˚C and is attributed to the removal of moisture absorbed at the time of loading the sample. Generally the irreversible degradation of PEO starts at 190 ˚C [27]. The degradation of PEO+LiTFSI+Cu-BDC MOF starts around at 310 ˚C. The enhanced thermal stability of Cu-BDC MOF added composite electrolytes may be attributed to the intercalation/exfoliation of the polymer matrix with MOF particles, which resulted in a strong barrier effect preventing from the thermal degradation to a certain extent and this observation is an indication of the fact that PEO+LiTFSI+ Cu-BDC MOF is stable up to a temperature of 300 ˚C in nitrogen atmosphere [28].

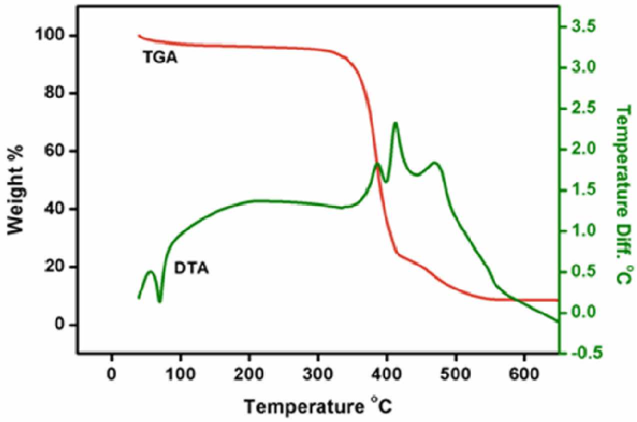

Figure 2. TG-DTA traces of composite polymer electrolytes.

Table 1. Composition of PEO, LiTFSI and Cu BDC MOF in (wt %)

S.L No.	Sample Code	PEO (wt.%)	Cu-BDC MOF (wt.%)	LiTFSI (wt.%)
1	S1	95	0	5
2	S2	93	2	5
3	S3	85	10	5
4	S4	80	10	10
5	S5	75	10	15

Tensile Strength

The stress-strain traces of sample S1 (95% PEO+5% LiTFSI) and S5 (75% PEO+10% Cu-BDC MOF+15% LiTFSI) are displayed in Figure 3. The tensile strength of sample S1 is 3.15 Mpa with an elongation-at-break value of 63%. Upon addition of 10% of Cu-BDC MOF in the PEO+LiTFSI complexes the elongation-at-break is increased to 162 % with a loss in the mechanical strength (1.15 MPa). This reduction in mechanical strength arises from the plasticization of PEO matrix by Cu-BDC MOF. A similar observation has been reported by Fan and Maier where the authors reported the mechanical properties of succinonitrile-added PEO+LiTFSI complexes [29]. However, the tensile strength of this composite polymer electrolyte is higher than that of MMT- modified carbon nanotube incorporated PEO- based electrolytes [30].

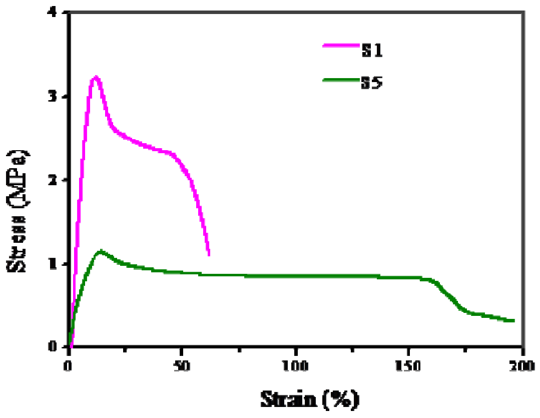

Figure 3. Stress *vs*. strain behavior of sample S1 and S5.

Ionic conductivity and charge-discharge studies

The ionic conductivities of composite polymer electrolytes for different proportions of PEO, LiTFSI and Cu-BDC MOF are depicted in Figure 4 in an Arrhenius plot. The ionic conductivity increases with the increase of temperature and also with the increase of Cu- BDC MOF content (samples S1 – S5). The ionic conductivity varies from 10^{-6} S cm^{-1} to 10^{-4} S cm^{-1} for the Cu-BDC MOF-free sample (S1). On the other hand, it varies from 10^{-6} S cm^{-1} to 10^{-3} S cm^{-1} when the content of Cu-BDC MOF was 10%. An increase in ionic conductivity of one order magnitude was observed at 30 ˚C and nearly two order magnitude was seen above 50 ˚C. The increase in ionic conductivity is observed for the Cu-BDC MOF added membrane (sample S5) at 0 ˚C which is very far from the glass transition temperature of PEO.

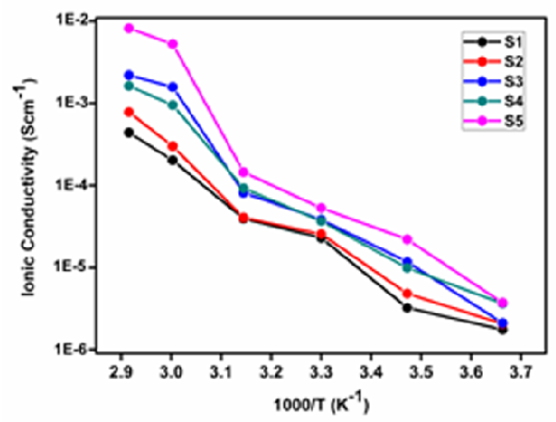

Figure 4. Ionic conductivity as a function of inverse temperature for the samples S1-S5.

A sharp change in the conductivity pattern is observed above 50 ˚C. Interestingly, the knee disappears above 50 ˚C suggesting the melting point and reduction in the degree of crystallinity of PEO and also promotes salt dissolution [2]. As commonly found in composite materials, the ionic conductivity is not a linear function of filler concentration. At low concentration levels the diffusion effect which, tends to depress conductivity, is effectively opposed by the specific interactions of the ceramic surfaces, which promote fast ion transport. At higher concentration dilution effect predominates and conductivity is reduced [31].

According to Scrosati and co-workers [32] based on their NMR studies, that the Lewis acid groups of the added inert filler may compete with the Lewis acid lithium cations for the formation of complexes with the alkoxide of PEO chains, as well as with anions of the added lithium salt. Subsequently, this makes structural modifications of the filler surfaces due to the specific actions of the polar surface groups of the inorganic filler. The Lewis acid-base interaction centers with the electrolytic species, lowers the ionic coupling and promotes the salt dissolution via a sort of “ion- filler complex” formation. In the present study, Cu BDC MOF (filler), which has Lewis acid center, can react with the anions of the lithium salt and these interactions lead to the reduction in the crystallinity of the polymer host. Very recently based on this type of Lewis-acid base interactions Zheng et al enhanced the performance of lithium sulfur batteries by the incorporation of nickel II-MOF in a polysulfide base [33]. Figure 5 illustrates the interaction of PEO chains with Cu-BDC MOF and LiTFSI.

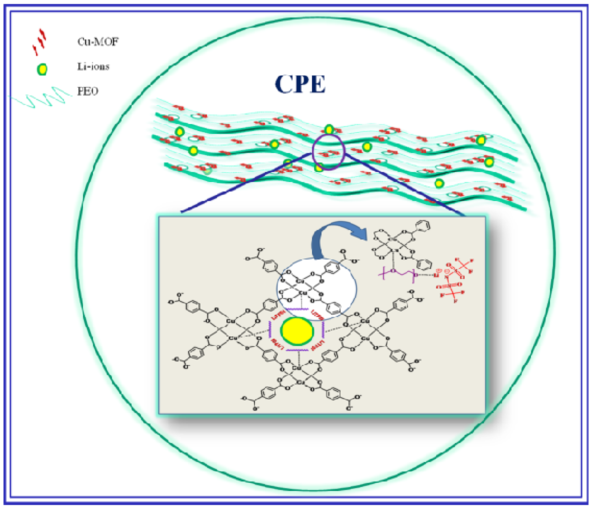

Figure 5. Schematic diagram of composite polymer Electrolyte and Cu-BDC MOF.

The lithium transference number, Li_t^+, plays a vital role on the performance and rate capability of lithium batteries for high power applications such as hybrid electric vehicles. In the present study lithium transference number was calculated using the equation (1).

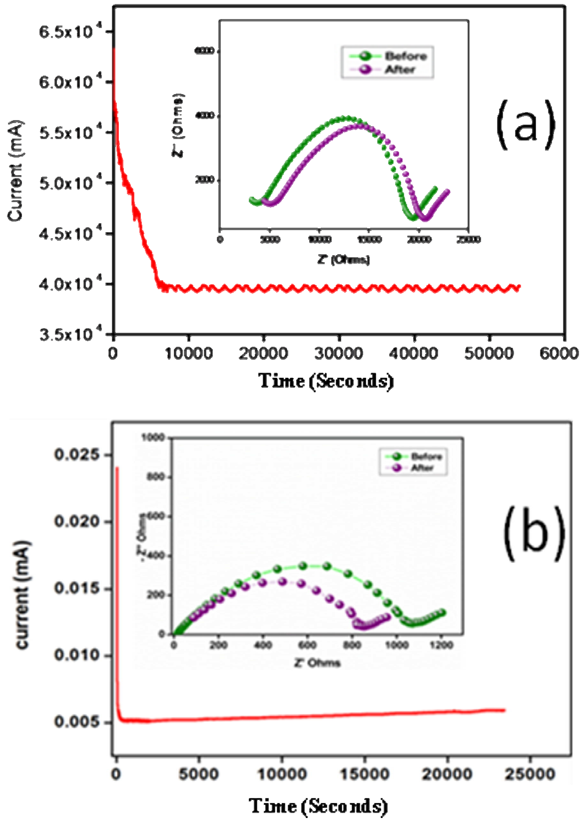

Figure 6 (a) Chronoamperometric measurements for the sample S1 and S5. Inset figure shows impedance spectra before and after perturbation.

Figure 6 (a & b) shows the chronoamperometric curve of samples S1 and S5 and inset shows the Nyquist plots before and after perturbation. It can be seen from the figure that there is no much difference between both curves (before and after perturbation) which further confirms the stability of the lithium electrode with the Cu-BDC MOF incorporated CPE. The value of Li_t^+ has been calculated as 0.1 and 0.41 for the samples S1 and S5 respectively. The value of 0.41 for sample S5 is sufficient for low C-rate applications [34].

Further in order to ascertain the usefulness of this CPE, the cycling studies have been made in a 2032-type coin cell. Figure 7 depicts the discharge capacity versus cycle number of Li/ CPE/$LiFePO_4$ cell at 70°C. In the present study, $LiFePO_4$ has been chosen as cathode material because of its appealing properties such as non-toxicity, thermal stability and environment friendly.

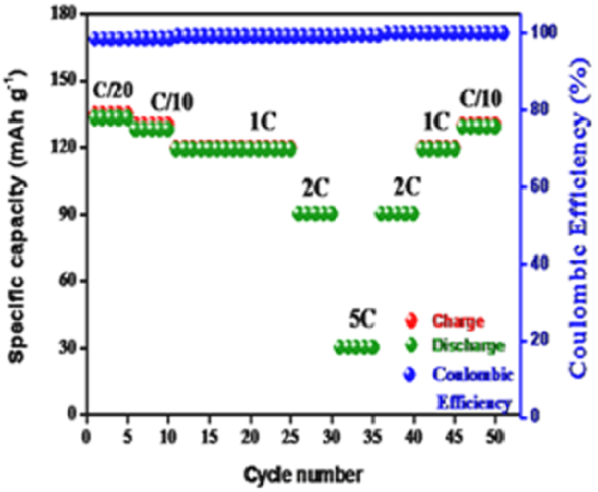

Figure 7. Discharge capacity *vs*. cycle number.

It is widely used as the ultimate choice of cathode material for nanocomposite polymer electrolyte system as it shows a flat operating voltage of 3.45 V *vs*. Li [25]. The cell delivered an initial discharge capacity of 132 mAh g^{-1} at C/20-rate and 126 mAh g^{-1} at C/10-rate without much fade in capacity. At 1C-rate the cell is able to deliver 120 mAh g^{-1} with 98% columbic efficiency.

The cell is able to deliver a specific capacity of 31 mAh g^{-1} even at 5C-rate.The reduction in the values of discharge capacity at higher C-rates is a typical characteristic of $LiFePO_4$ material which is attributed toits low electronic conductivity, limited diffusion of Li^+ ion into its structure that causes electrode polarization and solid electrolyte interface [35].

Further, the declining discharge capacity at higher C-rates may be due to the solid electrolyte interface (SEI) film formation with electrolyte decomposition. Recent study also revealed that the increase in interfacial resistance value which originates from parameters related to the electrode design such as thickness and density can cause capacity fading at higher rates [36]. It is also obvious from the figure that the cell restores its specific capacity again at 1C-rate from its 40th cycle indicating retention of structural stability of the cathode material.

Conclusions

The incorporation of Cu-BDC MOF in a PEO+LiTFSI matrix is an effective way to enhance the ionic conductivity and thermal stability of composite polymer electrolytes. It also promotes the elongation-at-break of polymer electrolytes. A better cyclability has been achieved due to higher ionic conductivity of the composite polymer electrolytes. The unique advantage of all solid-state-lithium polymer cells over its liquid counter part is that it can work at a higher temperature without any safety issues. The Li/CPE/$LiFePO_4$ cell is able to be cycled even at 70 ˚C which is superior to liquid electrolyte and thus guarantees for better safety.

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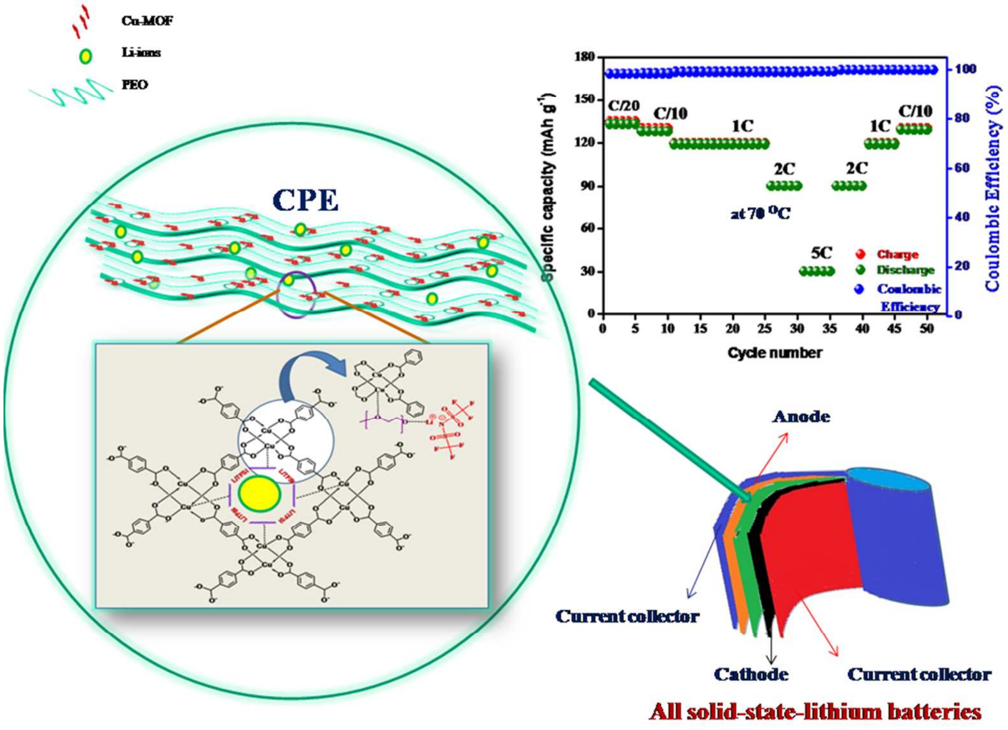

Graphical abstract
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