Chapter 6

Innovative High Performing MOF - Laden Composite Polymer Electrolytes for All Solid State Lithium Batteries
Chapter 6

6.1. Introduction

The unique properties such as high single cell voltage, energy density and long cycle life etc., have identified lithium-ion batteries as an ultimate power source for portable electronic devices such as laptop computers, cellular phones, digital camera etc.,.\(^1\) However the possible penetration of these lithium-ion batteries in to hybrid electric vehicle (HEV) and plug-in HEV can be realized only when substantial improvements such as low cost, safety, high rate capability and long calendar life are achieved.\(^2,3\)

The advancement in lithium battery technology relies mainly upon replacement of the conventional liquid electrolyte by an advanced solid polymer electrolyte. In order to achieve this goal, many lithium-conducting polymers have been prepared and characterised.\(^4\) Among the polymer hosts explored so far, the poly (ethylene oxide) (PEO) has been indeed the most extensively studied system.\(^5\) Unfortunately, these solid polymer electrolytes comprising a polymer host and a lithium salt (for e.g. PEO+LiClO\(_4\)) exhibit low ionic conductivity at ambient and sub-ambient temperatures.\(^6\) In fact, although PEO has several advantages like low cost, good chemical stability and safety, it exhibits appreciable ionic conductivity only above 70 °C which excludes it from ambient temperature applications.\(^1\) Numerous attempts have been made to enhance the ionic conductivity of PEO-based electrolytes, one of the most common way is the addition of low molecular weight liquid plasticizers like ethylene carbonate, propylene carbonate etc. The addition of plasticizers despite ameliorating the ionic conductivity, it adversely deteriorates the mechanical integrity and safety; moreover, side reactions with lithium metal eventually occur. In a pioneering research Weston and Steele\(^7\) have incorporated \(\alpha\)-alumina as a filler in a poly (ethylene oxide) and found an increase in the ionic conductivity of the composite system. Scrosati and co-workers demonstrated that the
filler acts as a solid plasticizer in the PEO matrix and inhibits the chain reorganization.\textsuperscript{8} This reorganization stabilizes the amorphous phase at lower temperature and thus providing a useful range of electrolyte conductivity. The degree of the reorganization depends upon the nature of the inert filler used.

Dispersion of nanosized ceramic fillers, such as TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, and SiO\textsubscript{2} in the polymeric matrix has significantly improved the ionic conductivity.\textsuperscript{9,10} By the addition of sulfate-promoted superacid zirconia (S-ZrO\textsubscript{2}) ceramic filler, a very high lithium transference number, $T_{\text{Li}^+} = 0.81 \pm 0.05$ has also been obtained, which is nearly twice the value of the ceramic-free electrolyte (0.42 \pm 0.05).\textsuperscript{11} The increase in the transport number values was attributed to the Lewis acid–base interactions occurring between the surface of the ceramic and both the X anion of the salt and the segments of the PEO chain. In an unconventional way of thinking, Bruce et al., illustrated the ionic conductivity in the crystalline complexes of PEO+LiXF\textsubscript{6} (where X =P, As, Sb).\textsuperscript{12} Recently, new interesting structures have been described in the literature as metal organic frameworks (MOFs).\textsuperscript{13,14} Generally speaking, they are microporous solids consisting of an infinite network of metal centers (or inorganic clusters) bridged by simple organic linkers through metal–ligand coordination bonds.\textsuperscript{15} MOFs are widely used in catalysis, sensors, ion exchange, gas storage, purification, separation and sequestration;\textsuperscript{16-22} they are also used in optoelectronics and to improve both electronic and proton conductivity.\textsuperscript{21} Recently, Wiers and co-workers demonstrated an increase in ionic conductivity of a solid electrolyte by adding lithium isopropoxide to a Mg-based metal organic framework followed by soaking in a conventional liquid electrolyte.\textsuperscript{23} Moreover, very recently Yuan et al., proposed a Zn-based MOF-5 as a novel filler for PEO-based composite polymer electrolytes showing improved electrochemical properties in Li-ion cells.\textsuperscript{24} Nevertheless, so far no attempt has
been made on the development of PEO-based composite polymer electrolytes (CPEs) encompassing an ad-hoc synthesised Al-BTC (aluminium benzenetricarboxylate) MOF and a proper lithium salt showing an ionic conductivity enhancement of more than two order of magnitude at low temperature and excellent stability towards lithium metal even after a prolonged storage time.

The obtained metal organic frameworks and macromolecular composite networks are thoroughly characterised from the structural morphological and physico-chemical viewpoint and, for the first time, an excellent long-term electrochemical behaviour in lab-scale LiFePO₄/CPE/Li cell is demonstrated (noteworthy stable even at 50 °C), thus accounting for the development of high performing, safe all-solid-state lithium batteries. Even though lots of literature data are available on ceramic based fillers, the studies based on MOF encompassed polymer electrolytes are truly interesting due to its tailor making capability and the broad spectrum of opportunities and possibilities it can bring. If very well tuned, the MOF based fillers will be a true promising candidate and a vital ingredient which can enforce the intrusion of polymer electrolytes into the huge market of Lithium based batteries.

6.2. Experimental Details

6.2.1. Materials

Al-plates with 99.9% purity (John Mathew, India) were used as the electrode materials. Benzene tricarboxylic acid (BTC, Acros organics, India), supporting electrolytes like TBAPC - Tetrabutylammonium tetrafluoroborate, TEATFB - Tetraethylammonium tetrafluoroborate, TBAPC - Tetrabutylammonium perchlorate. (Acros organics, India, analytical grade) and methanol (Sisco Research Laboratories,
HPLC grade) were used for synthesis of MOFs as received. Poly (ethylene oxide) (PEO, Aldrich, USA), lithium bis(trifluoromethanesulfonylimide)-LiTFSI (LiN(CF$_3$SO$_2$)$_2$, Merck, Germany) acetylene black (Shawinigan Black AB50, Chevron Corp., USA) acetonitrile (Sisco Research Laboratories, HPLC grade) and 1-methyl-2-pyrrolidone (NMP, Aldrich) were used for the preparation of membrane.

6.2.2. Experimental Procedure for the Synthesis of Al-BTC MOF

Two aluminium electrodes having similar area (10.5 cm$^2$) were used as the anode and the cathode for the synthesis of aluminium(III)-1,3,5-,benzenetricarboxylate (shortly, Al-BTC). Both the organic linker (0.1 M BTC) and the supporting electrolyte (TBAPC) were dissolved in 50 ml methanol solution in the electrolysis cell and stirred for 15 min for complete dispersion. The electrolysis was carried out in an electrochemical cell under constant voltage for 2.5 h to complete the reaction. Finally, the colourless precipitate of Al-BTC was collected from the electrolysis cell and allowed to dry in a hot air oven at 120 °C for 12 h and activated at 200 °C for 2 h. Further, optimisation of experimental parameters like supporting electrolyte concentrations, applied voltage and reaction time were carried out in order to get good yield and highly pure Al-BTC.

6.2.3. Characterisation Techniques

Powder X-ray diffraction (XRD) analysis was performed on a Xpert PROPAAnalytical PW3040/60‘X’PertPRO with Cu-Kα X-ray radiation source (λ = 1.5418 Å). Morphological characterisation of the Al-BTC products was performed employing a SEM Hitachi S-3000H scanning electron micro-scope (SEM, max magnification of 1.5 × $10^5$) equipped with an Everhardt Thornley secondary electron detector (ET-SED). Prior to analysis, all the samples were coated with a thin Au layer (around 10 nm thick) to minimize the effect of the electron beam irradiation. The EDX spectrum (Thermo
Electron Corporation, USA) was collected at an accelerating voltage of 20.0 kV at a magnification of $\times 700$.

The Brunauer-Emmett-Teller (BET) surface area and pore volumes (Barrett-Joyner-Halenda, BJH method) were evaluated by using nitrogen adsorption-desorption isotherms measured at 77 K on a ASAP 2020 V3.00H Micrometrics apparatus. Prior to adsorption, approximately 50.0 mg of solid were placed in the cell and evacuated at about 250 °C for 3 h.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a PHI Versa Probe 5000 (Physical Electronics) spectrometer on pelletized samples with a pass energy of 23.5 eV using the Al-K$\alpha$ as the exciting source of the X-ray. The internal correction of the binding energy was done using the adventitious C 1s peak near 284.5 eV. The thermal stability of the samples was tested by thermo-gravimetric analysis (TGA), with a Q 500 instrument from Mettler, over a temperature range of 25-1000 °C under N$_2$ flux at a heating rate of 10 °C min$^{-1}$. The glass transition temperature ($T_g$) of the materials was evaluated by differential scanning calorimetry (DSC) with a METTLER DSC-30 instrument, equipped with a low temperature probe.

Solid-state MAS-NMR spectra were acquired on a 400 MHz spectrometer (Bruker) using a 4 mm MAS probe (Bruker). $^7$Li spectra were acquired with a single-pulse sequence, MAS frequency of 11 kHz, using a 90° pulse of 5 $\mu$s, a recycle time of 0.5 s, and averaging over 2k acquisitions. The chemical shift reference is 1.0 M LiCl. $^{27}$Al spectra were acquired with a single-pulse sequence, MAS frequency of 11 kHz, using a hard pulse of 1 $\mu$s, a recycle time of 0.5 s, and averaging over 4k acquisitions. The chemical shift reference is Al$^{3+}$ in aqueous solution. $^{13}$C,$^1$H CP-MAS spectra were
acquired at MAS frequency of 11 kHz, with a contact time of 3 ms, and a recycle time of 2 s. The chemical shift reference is tetramethyl silane (TMS). The spectra were analyzed with TopSpin package (Bruker).

The Fourier transform infrared spectroscopy (FT-IR, ThermoNICOLET Corporation, 5DX-FT-IR) was made at ambient temperature with a 8 cm\(^{-1}\) resolution. The final thickness of the membranes was measured with a Mitutoyo Series 547 Thickness Gauge, equipped with an Absolute Digimatic Indicator (model IDC112XBS), with a resolution of ±1 \(\mu\)m and a maximum measuring force of 1.5 N.

The ionic conductivity of the CPEs, sandwiched between two stainless steel (SS-316) blocking electrodes (1 cm\(^2\) diameter), configuration SS-316/CPE/SS-316, was measured using an electrochemical impedance analyzer (BAS IM6 Analytical Systems) in the 50 mHz to 100 kHz frequency range at various temperatures, from 20 to 80 °C. Symmetric non-blocking cells of the type Li/CPE/Li were assembled for compatibility studies (interfacial stability), which was investigated by studying the time dependence of the impedance of the systems under open-circuit potential at 60 °C.

6.2.4. Electrode Preparation, Lithium Cell Assembly and Electrochemical Characterisation

The LiFePO\(_4\)/C cathode material was synthesised in the form of nanostructured powder through a mild hydrothermal procedure previously described in Meligrana et al.,\textsuperscript{25} The composite cathode was prepared in the form of a film (average thickness of about 70 \(\mu\)m, calculated active material weight of about 2 mg) by blending 8 wt% of poly(vinylidene fluoride) as the binder (Solvay Solef 6020) with 10 wt% of acetylene black as the electronic conductivity enhancer and 82 wt% of LiFePO\(_4\)/C active material,
thoroughly mixed in 1-methyl-2-pyrrolidone. The paste was coated by a doctor-blade process onto an aluminum foil current collector. After the complete evaporation of the NMP solvent by mild heating and progressive vacuum treatment for 24 h, electrode disks of 2.54 cm² were punched out and dried under high vacuum at 130 °C for 5 h.

The lithium polymer cells for the evaluation of the electrochemical characteristics were fabricated by laminating the three components in sequence, i.e., a lithium metal anode foil, a layer of the CPE membrane and the LiFePO₄/C composite cathode film. The assembly was housed into a hermetically sealed test cell (model ECC-Std, http://el-cell.com/products/test cells/ecc-std, purchased from EL-Cell, Germany). All preparations were performed in an argon-filled dry glove box (MBraun Labstar, Germany) having a humidity content below 1 ppm. The characteristics and performance of the all-solid lithium polymer cell were investigated at 50, 60 and 70 °C in terms of charge/discharge galvanostatic cycling by an Arbin Instrument Testing System model BT-2000, setting the cut off voltages to 2.50 - 4.00 V vs. Li⁺/Li, setting the charge–discharge cycles at the same rates, ranging from C/10 to 5 C (calculated on the basis of the theoretical specific capacity of 170 mA h g⁻¹ for LiFePO₄). Charge reaction corresponds to the lithium de-intercalation from the electrode material structure while discharge reaction corresponds to the lithium intercalation into the electrode material structure.

Impedance spectra were made before and after the pulse application in order to evaluate the changes. Clean electrodes and fresh samples were used for each of the above reported tests. To confirm the results obtained, the tests were performed at least three times on different fresh cells.
6.3. Results and Discussion

6.3.1 Optimisation of Electrolysis Conditions

*Fig. 6.1. Hypothetical network structure of aluminium(III)-1,3,5-benzenetricarboxylate (namely, Al-BTC) metal organic framework a) ball & stick model and b) polyhedral model.*
Al-BTC MOF was synthesised by an electrolytic process and its hypothetical structure is schematised in Fig. 6.1. Details of the preparation procedure for the synthesis of MOF powder is already presented in experimental part. The reaction scheme for synthesis of Al-BTC is presented as Scheme 6.1.

Scheme 6.1. Reaction scheme for the synthesis of Al-BTC from Al and 1,3,5-benzene tricarboxylic acid.

The experimental reaction condition was optimized by different parameters such as effect of supporting electrolyte, supporting electrolyte concentration, BTC concentration and applied cell potential are presented in Table 6.1. Fig. 6.2 depicts the effect of reaction time vs. yield (blue colour) and reaction time vs. current (red colour). The yield mainly depends on reaction time but as the reaction time goes on the availability of BTC decreases and thereby current decreases. The criteria for optimized electrochemical condition in order to get maximum yield, high surface area, controlled Al dissolution and high purity without agglomeration. The optimised reaction condition is 0.1 M BTC (organic ligand), 0.1 M TBAPC (supporting electrolyte), 15 V applied cell
potential and reaction time 150 min. The obtain yield of the product corresponding to the amount of weight loss in the aluminium anode is 93.4%.

Table 6.1 Experimental parameters for optimisation of reaction condition.

<table>
<thead>
<tr>
<th>S.L No.</th>
<th>Supporting Electrolyte</th>
<th>Supporting Electrolyte Concentration (M)</th>
<th>BTC Concentration (M)</th>
<th>Applied Cell Potential (V)</th>
<th>Yield (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TBATFB</td>
<td>0.1</td>
<td>0.1</td>
<td>15</td>
<td>0.57</td>
</tr>
<tr>
<td>2</td>
<td>TEATFB</td>
<td>0.1</td>
<td>0.1</td>
<td>15</td>
<td>No reaction</td>
</tr>
<tr>
<td>3</td>
<td>TBAPC</td>
<td>0.1</td>
<td>0.1</td>
<td>15</td>
<td>3.36</td>
</tr>
<tr>
<td></td>
<td><strong>Effect of Supporting Electrolyte concentration</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>TBAPC</td>
<td>0.02</td>
<td>0.1</td>
<td>15</td>
<td>0.32</td>
</tr>
<tr>
<td>5</td>
<td>TBAPC</td>
<td>0.04</td>
<td>0.1</td>
<td>15</td>
<td>0.75</td>
</tr>
<tr>
<td>6</td>
<td>TBAPC</td>
<td>0.05</td>
<td>0.1</td>
<td>15</td>
<td>2.78</td>
</tr>
<tr>
<td>7</td>
<td>TBAPC</td>
<td>0.2</td>
<td>0.1</td>
<td>15</td>
<td>1.93</td>
</tr>
<tr>
<td></td>
<td><strong>Effect of BTC Concentration</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>TBAPC</td>
<td>0.1</td>
<td>0.05</td>
<td>15</td>
<td>1.52</td>
</tr>
<tr>
<td>9</td>
<td>TBAPC</td>
<td>0.1</td>
<td>0.15</td>
<td>15</td>
<td>3.19</td>
</tr>
<tr>
<td></td>
<td><strong>Effect of Applied Cell Potential</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>TBAPC</td>
<td>0.1</td>
<td>0.1</td>
<td>5</td>
<td>0.56</td>
</tr>
<tr>
<td>11</td>
<td>TBAPC</td>
<td>0.1</td>
<td>0.1</td>
<td>10</td>
<td>1.67</td>
</tr>
<tr>
<td>12</td>
<td>TBAPC</td>
<td>0.1</td>
<td>0.1</td>
<td>12.5</td>
<td>1.92</td>
</tr>
<tr>
<td>13</td>
<td>TBAPC</td>
<td>0.1</td>
<td>0.1</td>
<td>17.5</td>
<td>1.95</td>
</tr>
</tbody>
</table>

TBAPC - Tetrabutylammonium tetrafluoroborate, TEATFB - Tetraethylammonium tetrafluoroborate, TBAPC – Tetrabutylammonium perchlorate.
Fig. 6.2. The plots corresponding to the reaction time vs. yield and reaction time vs. current.

6.3.2. Characterisation of Synthesised Al-BTC MOF

To understand the nature of chemical bonding between benzene tricarboxylic acid and Al$^{3+}$ ion, FT-IR spectral analysis was carried out and is shown in Fig. 6.3. The main characteristic vibration band observed at 1716 cm$^{-1}$ can be significantly assigned to acidic carbonyl C=O stretching vibration of BTC molecule, which is shifted to 1625 cm$^{-1}$ is ascribed to the interaction of BTC molecule with Al$^{3+}$ particularly it suggest that acidic C=O group undergo deprotonation and interact with Al$^{3+}$ ions. This unambiguously indicates that the carboxylate ion participates in the complex formation with Al$^{3+}$ ion. Moreover, the characteristic vibration at 726 cm$^{-1}$ may be attributed to Al-O stretching vibration, in which the oxygen atom is co-ordinated with Al.$^{26}$
Fig. 6.3. FT-IR analysis of Al-BTC MOF.

Fig. 6.4. SEM analysis of as-synthesised Al-BTC MOF (a) and Al-BTC after ultrasonic treatment (b).

Fig. 6.4. shows the morphological structure (SEM image) of the electrochemically synthesised Al-BTC MOF sample at optimized experimental reaction condition. Morphological studies clearly show that as synthesised Al-BTC exhibit the agglomerated
amorphous structure. After ultrasonic treatment with excess acetone solvent the amorphous structure undergo the particle nature.

![Graph showing XRD analysis](image)

**Fig. 6.5. Powder XRD analysis of Al-BTC MOF.**

The phase purity of the synthesised Al-BTC MOF was characterised by powder X-ray diffraction (XRD) analysis, the wide-angle XRD pattern is shown in Fig. 6.5. Obviously, two well-defined diffraction peaks are observed at 2θ values of 9.6° and 25.5°, respectively. In addition to that, the chemical composition and the purity of electrochemically synthesised Al-BTC was determined using energy dispersive X-ray analysis as shown in Fig. 6.6. It clearly shows the presence of Al, no other peaks of impurities can be found than that of carbon and oxygen. The effective atomic weight percentage of Al, C, and O are listed in the Table 6.2. Since there are no peaks corresponding to nitrogen and chloride, here we conclude that electrochemically synthesised Al-BTC does not contain any impurities (like supporting electrolyte TBAPC).
Fig. 6.6. Energy dispersive X-ray analysis spectrum of Al-BTC MOF.

Table 6.2. Element composition of Al-BTC MOF from EDX analysis

<table>
<thead>
<tr>
<th>S.L No.</th>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>% of C</td>
<td>34.27</td>
</tr>
<tr>
<td>2</td>
<td>% of O</td>
<td>49.46</td>
</tr>
<tr>
<td>3</td>
<td>% of Al</td>
<td>16.27</td>
</tr>
</tbody>
</table>

To find out the exact specific pore volume and surface area of electrochemically synthesised and activated Al-BTC, the BET and Langmuir nitrogen gas adsorption/desorption isotherm studies were carried out. The nitrogen adsorption data yield a specific pore volume, pore size, surface area and are presented in Table 6.3. Porous nature is confirmed from the steep rise at the high relative pressure in the isotherm and also the average particle size is found to be 50.06 nm. X-ray photoelectron
spectroscopy is carried out on the particles recovered after the ultrasonic treatment, which is shown in Fig. 6.7. The main peaks observed in the survey scan as Al2p$_{3/2}$, at 75.25 eV is confirmed the oxidation state of aluminium as Al$^{3+}$ trivalent state. The binding energy of C1s emission peak observed at 284.5 eV, which was used as the reference in the present XPS measurements.

Table 6.3. List of the porous and surface properties of Al-BTC MOF.

<table>
<thead>
<tr>
<th>Pore Volume</th>
<th>Average pore Radius</th>
<th>Pore Size (width)</th>
<th>BET surface Area</th>
<th>Langmuir surface Area</th>
<th>Average Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.52 cm$^3$ g$^{-1}$</td>
<td>16.3 nm</td>
<td>53.56 nm</td>
<td>520 m$^2$ g$^{-1}$</td>
<td>695 m$^2$ g$^{-1}$</td>
<td>50.06 nm</td>
</tr>
</tbody>
</table>

Fig. 6.7. X-Ray photoelectron spectroscopy of Al-BTC MOF.
The nature of thermal stability and the molecules that are desorbed or buried in the synthesised Al-BTC with respect to temperature was studied by TGA analysis in nitrogen atmosphere with a heating rate of 5 °C min\(^{-1}\) and is presented in Fig. 6.8. The thermogram shows two different regions viz., 1) the first weight loss region between 50 and 250 °C indicating the loss of moisture and solvent molecules 2) the second region starts at 437 °C, at that temperature the structure of MOF collapse and the organic linker is buried. This weight loss is completed at 665 °C and stable up to 1000 °C, the residue is found to be 15.6%.

![Thermal gravimetric curve of Al-BTC MOF.](image)

**Fig. 6.8.** Thermal gravimetric curve of Al-BTC MOF.

### 6.3.3. Thermal analyses of Al-BTC MOF-Polymer Composite Membrane

For the preparation of all-solid-state composite polymer electrolytes, polyethylene oxide (PEO) and lithium bis(trifluoromethanesulphonimide)-LiTFSI (LiN(CF\(_3\)SO\(_2\))\(_2\)), were dried under vacuum for 2 days at 50 and 100 °C, respectively,
before use. Al-BTC was also dried under vacuum at 50 °C for 5 days before use. Composite polymer electrolytes (CPEs) were prepared by dispersing appropriate amounts of Al-BTC in the PEO-LiN(CF$_3$SO$_2$)$_2$ mixture (see Table 6.3 for the list and compositions of samples prepared) and hot-pressing into films as detailed by Appetecchi et al.$^{28}$ The complete dispersion was achieved by mechanical mixing with Ultra-Turrax for 3 min. The CPE 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 characterisation. Five different composite polymer electrolyte membranes encompassing Al-BTC metal organic frameworks were prepared, with varying amounts of PEO, Al-BTC and LiTFSI salt, respectively, as shown in Table 6.4.

**Table 6.4.** List of the samples prepared along with their compositions expressed in weight percent (wt.%) of the total weight.

<table>
<thead>
<tr>
<th>S.L No.</th>
<th>Sample Code</th>
<th>Polymer wt.%</th>
<th>Al-BTC MOF wt.%</th>
<th>LiTFSI wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S1</td>
<td>95</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>S2</td>
<td>93</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>S3</td>
<td>85</td>
<td>10</td>
<td>5</td>
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<tr>
<td>4</td>
<td>S4</td>
<td>80</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>S5</td>
<td>75</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>

Differential Scanning Calorimetry (DSC) measurements were carried out in order to identify the extent of intercalation and exfoliation of the fillers in the CPEs. Fig. 6.9. shows the DSC thermograms of the composite polymer electrolytes measured from -100 to +100 °C. The melting point of the PEO+LiTFSI electrolyte was increased from 59 to
66 °C upon addition of MOF in the polymeric matrix. Similarly, the glass transition temperature \( T_g \) was also increased from -54 to -48 °C. The \( T_g \) increase of the CPE with respect to the PEO might be due to (i) the effect of a small amount of dispersed particles and (ii) confinement of the intercalated/exfoliated polymer chains within the filler galleries, which resists the segmental motion of the polymer chains.\(^\text{29}\) In particular, the increase in the \( T_g \) value of CPEs (towards the positive side) indicates better polymer–filler interaction, while the decrease in \( T_g \) (towards the negative side) indicates the plasticization effect. The marginal decrease in the melting point of the PEO polymer at higher concentration of fillers is attributed to the mild retarding effect on the crystallization that arises due to the added filler/MOF particles.\(^\text{30}\)

Fig. 6.9. DSC traces of PEO, PEO+Al-BTC, PEO+LiTFSI and the composite polymer electrolyte PEO+Al-BTC+LiTFSI.

The thermo-gravimetric traces of PEO+LiTFSI+Al-BTC MOF (sample S4) are depicted in Fig. 6.10. A small endothermic peak that appears around 42 °C with a
corresponding weight loss of less than 2% is attributed to the removal of moisture absorbed at the time of loading the sample.\textsuperscript{31} Another endothermic peak that appears around 70 °C is due to the melting of PEO.\textsuperscript{32,33} No further appreciable weight losses were absorbed until the irreversible decomposition which starts at 345 °C. This confirms that the composite polymer electrolyte membrane is thermally stable up to this high temperature, at least in nitrogen atmosphere, which is fairly higher than the normal operating temperature of lithium batteries. The increase in the thermal stability of the composite polymeric membrane was attributed to the intercalation/exfoliation of the polymer matrix with inert particles, which resulted in a strong barrier effect preventing from the thermal degradation to a certain extent.\textsuperscript{33}

Fig. 6.10. Thermo-gravimetric analysis, under N\textsubscript{2} flow in the temperature range 25–1000 °C of sample S4.
6.3.4. Ionic Conductivity Studies

In order to employ the polymer electrolytes in all-solid-state lithium polymer batteries, the ionic conductivity was measured for the samples prepared with various concentrations of lithium salt, LiTFSI and MOF. Generally, LiTFSI salt is prone to corrode the aluminium current collector.\textsuperscript{34} Thus, in the present study, CPEs were prepared by limiting the maximum concentration of lithium salt to 10-15 wt.%, in order to obtain the optimal compromise between high ionic conductivity and negligible corrosion of the aluminium current collector.\textsuperscript{35} Fig. 6.11. illustrates the variation of ionic conductivity as a function of $1/T(K)$ for the CPEs having different content of lithium salt and MOF. It can be seen that the ionic conductivity increases with the increase of MOF content (samples S1 to S4) and for the lithium salt content up to 10 wt.%. It starts decreasing with the further increase of lithium salt content (15 wt.%, sample S5). The reduction in ionic conductivity is attributed to the increase in the viscosity of the polymer solution.\textsuperscript{36,37} The ionic conductivity ranges from $10^{-8}$ to $10^{-4}$ S cm\textsuperscript{-1} for sample S1 (only PEO+LiTFSI) between 20 and 80 °C. Upon a limited addition of 2 wt.% of Al-BTC MOF in the polymeric matrix, an increase in ionic conductivity nearly of one order of magnitude is observed. However, when the content of MOF and lithium salt are both increased to 10 wt% (sample S4), the ionic conductivity is outstandingly increased by more than two orders of magnitude at 20 °C.

As commonly found in composite materials, the ionic conductivity is not a linear function of the filler concentration\textsuperscript{5}. At low concentration levels the diffusion effect which, tends to depress the conductivity, is effectively opposed by the specific interactions of the ceramic surfaces, which promote fast ion transport. Hence, an apparent enhancement in conductivity is seen in both cases. At higher filler content, the dilution
effect predominates and the conductivity is lowered. On the other hand, when the concentration of the filler is increased, the dilution effect predominates and the conductivity decreases.\textsuperscript{36} Thus, the maximum conductivity is generally achieved only in the concentration region 8-10 wt%. According to Croce and co-workers from their NMR studies, the local dynamics of the lithium ions, in particular lithium mobility is not changed by the filler, thus supporting the idea that the enhancement of conductivity by adding a filler is caused by stabilizing and increasing the fraction of amorphous phase.\textsuperscript{37} 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 the anions of the added lithium salt.

![Fig. 6.11. Ionic conductivity Arrhenius plot as a function of temperature of the different samples prepared. Data derived from impedance spectroscopy.](image)

Subsequently, this results in 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 centre’s with the electrolytic species, thus lowering the ionic coupling and promotes the salt dissociation via a sort of “ion-filler complex” formation. In the present study, Al-BTC (filler), which has Lewis acid centre, can react with the anions of the lithium salt and these interactions lead to the reduction in the crystallinity of the polymer host. Indeed, this effect could be the reason for the observed remarkable enhancement in the ionic conductivity.  

6.3.5. Interfacial Properties

A deep understanding of the interfacial properties between lithium metal and polymer electrolyte is mandatory in order to provide more insight into the factors controlling the recharge ability of lithium-based polymer batteries. It is well known that the lithium surface is normally almost covered by a passive layer called solid electrolyte interface (SEI) and this layer is believed to play a key role in the electrochemical performance of lithium batteries as far as the calendar life is concerned. Many experimental techniques, such as XPS, infrared spectroscopy, NMR, in-situ synchrotron X-ray reflectometry, and ellipsometry have been employed to study the nature and formation mechanism of the SEI layer. Many reasons have been suggested for poor cycling of lithium cells, which include electrochemical reactions between the anode and the electrolyte and loss of electronic contact between the electrode and dendritic lithium. In the polymer electrolyte systems, on the other hand, a resistive layer covers the lithium metal electrode and the resistance of this layer grows with time, possibly reaching values over 10 kΩ cm⁻². The nature of this layer depends mainly on the purity and composition of the electrolyte.

In the present study, the compatibility (interfacial stability) studies have been examined with proper attention on the newly elaborated PEO composite membranes.
Sample S4 was examined as this composition was found to be optimal from the point of view of the ionic conductivity. Fig. 6.12 displays the variation of interfacial resistance, \( R_i \), as a function of time for the Li/S3-CPE/Li symmetric cells kept under open circuit condition at 60 °C. As described by Abraham and co-workers, the interfacial resistance can be measured from the Cole–Cole impedance plots (not shown in the figure) in which the large semi-circles represent a parallel combination of resistance (\( R_{\text{film}} \)) and capacitance associated with the passivation film on the Li metal electrode.\(^{45}\) A small semicircle is due to the charge transfer resistance in parallel with the double layer capacitance. The intercept of the large semi-circle at high frequency on the Z-axis is mostly associated with the interfacial resistance “\( R_i \)” of the system. It is observed from the figure that the composite polymer electrolyte containing the Al-BTC MOF filler is definitively more compatible than the polymer electrolyte prepared by only PEO and LiTFSI, being lithium metal used as the anode.

**Fig. 6.12.** Variation of interfacial resistance (\( R_i \)) as a function of time for the symmetric cells composed of Li/S4-CPE/Li and Li/S1/Li both stored at 60 °C.\(^{45}\)
As clearly evident, in the case of sample S4 the resistance values do not change much even after 300 h. This may be explained by assuming that the morphology of the passivation film changes with time to finally acquire a noncompact, possibly porous structure. Furthermore, it is quite obvious from the figure that the overall interfacial resistance of the polymer host has been considerably reduced upon the incorporation of the inert filler (much lower than the filler-free membrane).

6.3.6. Lithium Transference Number

Generally speaking, the nanosized inert fillers are more compatible than the micron-size ones. The inert particles, depending upon their volume fraction, would tend to minimize the area of the lithium electrode exposed to polymers containing −O− and −OH species, thus reducing the passivation process. It is also foreseeable that lower sized particles for a similar volume fraction of the ceramic phase would impart an improved performance as compared to larger sized particles because they will cover more surface area. The formation of an insulated layer of ceramic particles at the electrode surface is probable at a higher volume fraction of a passive ceramic phase. This insulating layer will impede electrode reactions. This may very well have happened in the present system when 10 wt.% of the ceramic phase was introduced into the polymer matrix.

The lithium transference number, \( \text{Li}^+ \), is a key factor in the optimisation of electrolytes for lithium batteries. Indeed, high \( \text{Li}^+ \) guarantees high enough power density. In our present newly elaborated composite polymer system encompassing Al-BTC MOF, the \( \text{Li}^+ \) was found to be reasonably high, which is 0.55 according to the profile graph presented in Fig. 6.13.

The lithium transference number was calculated by the method proposed by Vincent and co-workers. The following formula was adopted.
\[ \text{Li}^+ = \frac{I_{ss}(V-I_0R_0)}{I_0(V-I_{ss}R_{ss})} \]

The Li/CPE/Li cell was polarized by a dc pulse of 10 mV. Time evolution of the resulting current flow was then followed. The initial \((I_0)\) and steady state \((I_{ss})\) values of current flowing through the cell during the polarization were measured. \(R_0\) and \(R_{ss}\) represent the resistance values before and after the perturbation of the system.

![Graph](image)

**Fig. 6.13.** Li transference number profile graph of PEO+MOF+LiTFSI.

### 6.3.7. Solid-State NMR Studies

Multinuclear solid-state NMR analyses and Fourier Transform Infrared Spectroscopy (FT-IR) were used to evidence the possible interaction of MOF with PEO and lithium. The \(^{27}\text{Al} \text{MAS}\) spectra of the samples Al-MOF, PEO+Al-MOF and PEO+LiTFSI+Al-MOF are presented in Fig. 6.14. All the spectra show a main feature at 0 ppm due to aluminium in octahedral coordination, whose right asymmetry is attributed to statistical disorder.\(^{50,51}\) Two other peaks, accounting for few percent, are observed at 35 and 65 ppm, and can be attributed to aluminium coordinated to five and four oxygen
atoms, respectively. These last peaks are likely due to surface defects of the MOF particles and, interestingly, their amount increases in the sample PEO+LiTFSI+Al-MOF probably due to the preparation procedure. Fig. 6.15 shows the $^7$Li MAS spectra of the samples PEO+LiTFSI and PEO+LiTFSI+Al-MOF. In both cases, the observed spectral lines are in the motionally narrowed regime, which means that the correlation rate for Li motion, $\tau_c^{-1}$, is of the order of the Larmor frequency, and that only the Hamiltonian isotropic contributions are retained. Therefore, the structure observed in the spectrum of PEO+LiTFSI is due to the presence of Li ions in different chemical environments, which are not time-averaged by spin motion during the NMR experiment. Four contributions are found at -0.50, -0.81, -0.97, -1.09 ppm. The addition of MOF caused a further narrowing of the line, which assumes a Lorentzian shape (typical of liquid-like motion) with a chemical shift of -0.87 ppm, roughly corresponding to the centre-of-mass of the four contributions previously described.

![Solid state NMR $^{27}$Al MAS spectra](image)

**Fig. 6.14.** Solid state NMR $^{27}$Al MAS spectra of a) Al-MOF, b) PEO+Al-MOF and c) PEO+LiTFSI+Al-MOF respectively. *spinning sidebands.*
**Fig. 6.15.** Solid state NMR $^7$Li MAS spectra of a) PEO+LiTFSI and b) PEO+LiTFSI+Al-MOF respectively.

**Fig. 6.16.** Solid state NMR $^{13}$C MAS spectra of a) Al-MOF, b) PEO+Al-MOF, c) PEO+LiTFSI and d) PEO+LiTFSI+Al-MOF respectively.
Therefore the role of MOF is to plasticise the structure which is in agreement with the DSC results, and to improve the Li$^+$ ion mobility. Finally, the 13C CP-MAS spectra of MOF, PEO+MOF, PEO+LiTFSI, and PEO+MOF+LiTFSI are shown in Fig. 6.16. Summarising, from the analysis of the NMR data, it is not possible to clearly unravel the interactions among MOF, polymer and lithium salt.

6.3.8. FT-IR Analysis

FT-IR has been identified as a powerful tool to study the complexation between salts and polymers as it is sensitive to molecular and structural changes in the polymer systems. The FT-IR spectra of PEO, Al-BTC, PEO+LiN(CF$_3$SO$_2$)$_2$ and PEO+LiN(CF$_3$SO$_2$)$_2$+Al-BTC are displayed in Fig. 6.17(a–d). The band that appears at 2886 cm$^{-1}$ is attributed to asymmetric stretching mode and the peak at 1967 cm$^{-1}$ to a symmetric mode. The peaks at 1466, 1103, 956 and 841 cm$^{-1}$ are assigned to $\text{CH}_2$–scissoring, $\text{C}–\text{O}–\text{C}$– stretching, $\text{CH}_2$ twisting and $\text{CH}_2$– wagging modes, respectively. Also, PEO exhibits $\text{C}–\text{H}$ stretching (between 2800 and 2935 cm$^{-1}$), asymmetric stretching (1950–1970 cm$^{-1}$), asymmetric bending (1450 cm$^{-1}$), $\text{CH}_2$ scissoring (1465–1485 cm$^{-1}$), $\text{C}–\text{O}$–$\text{O}$ stretching (1250–950 cm$^{-1}$), $\text{CH}_2$–twisting (991 cm$^{-1}$) and $\text{CH}_2$– wagging (842 cm$^{-1}$). The band that appears at 2886 cm$^{-1}$ can be assigned to the $\text{C}–\text{H}$ stretching mode, and the peak at 1967 cm$^{-1}$ is due to an asymmetric stretching mode. The peaks at 1466, 1103, 956, and 841 cm$^{-1}$ are assigned to $\text{CH}_2$– scissoring, $\text{C}–\text{O}–\text{C}$– stretching, $\text{CH}_2$– twisting and $\text{CH}_2$– wagging modes, respectively.$^{54-56}$ Also, PEO exhibits $\text{C}–\text{H}$– stretching (between 2800 and 2935 cm$^{-1}$), asymmetric stretching (1950–1970 cm$^{-1}$), asymmetric bending (1450 cm$^{-1}$), $\text{CH}_2$ scissoring (1465–1485 cm$^{-1}$), $\text{C}–\text{O}$–$\text{O}$ stretching (1250–950 cm$^{-1}$), $\text{CH}_2$– twisting (991 cm$^{-1}$), and $\text{CH}_2$– wagging (842 cm$^{-1}$).$^{57,58}$ In particular, we observed that the strongest peak, $\text{C}–\text{O}–\text{C}$ at 1104 cm$^{-1}$, of PEO is shifted
to 1106 cm\(^{-1}\) in the complex upon incorporation of LiTFSI (Fig. 6.17c). The intensity of the peak is further reduced when both Al-BTC and LiTFSI are laden together (Fig. 6.17d).

![Figure 6.17](image)

**Fig. 6.17.** Comparison of the FT-IR analyses on PEO, Al-BTC, PEO+Al-BTC and PEO+Al-BTC+LiTFSI, respectively.

The reduction in the intensity of the peak was ascribed to the complex formation between PEO, Al-BTC and LiTFSI. In a similar way, a reduction in the peak has been observed for –CH\(_2\) twisting at 955 cm\(^{-1}\) and C–H stretching band centered around 2900 cm\(^{-1}\). A similar observation has been reported by Manuel Stephan et al. where the authors reported the interaction between PEO and lithium salts along with chitin filler.\(^{53,59}\)
6.3.9. Cycling Studies of LiFePO₄/Al-BTC-NCPE/Li Cells

In order to demonstrate the feasibility of the novel Al-BTC MOF-laden PEO-based electrolytes, sample S4 was assembled in a lab-scale lithium cell, sandwiched between a LiFePO₄/C composite cathode and a lithium metal anode and its electrochemical behaviour tested at different temperatures and different current rates upon long-term cycling. Compared with conventional layered cathode materials based on transition metal oxides widely used in Li-ion batteries, LiFePO₄ was chosen due to its unique properties such as thermal stability, non-toxicity, eco-friendliness, cost-effectiveness and easy preparative methods. Moreover, it was identified as the ultimate choice as cathode material for nanocomposite polymer electrolyte systems, showing a flat operating voltage of 3.45 V vs. Li and good discharge capacity at low C-rates. In particular, we decided to use a hydrothermally synthesised LiFePO₄ developed in our Labs because of the ready availability and the overall reasonably good performances.

The results of the galvanostatic charge/discharge cycling in lab-scale lithium cell are plotted in Fig. 6.18(a-c). It shows typical charge and discharge profiles vs. specific capacity at 1C rate and 70 °C (Fig. 6.18a), the specific capacity as a function of the cycle number at 70 °C and different current regimes from C/10 to 5C (Fig. 6.18b) and the specific capacity as a function of the cycle number at 1C rate and different temperatures (Fig. 6.18c). The cell operates with the expected potential profiles: typical charge and discharge potential versus time profiles between 3.0 and 3.8 V vs. Li at 1C rate show highly reproducible and well defined plateaus at about 3.48 V vs. Li upon charge (delithiation) and about 3.37 V vs. Li upon discharge (lithiation), which are well in agreement with the characteristic behaviour upon reversible redox reaction with lithium of LiFePO₄ electrodes.
Fig. 6.18. Electrochemical characteristics of the LiFePO₄/S4-CPE/Li cell at different temperatures and current regimes. a) Typical potential vs. time profiles at 70 °C and 1C rate; b) Galvanostatic discharge/charge cycling test at fixed 70 °C and varying C-rates (from C/10 to 5C) along with the Coulombic efficiency and c) prolonged galvanostatic cycling at fixed 1C rate and varying temperatures along with the Coulombic efficiency.

The cell demonstrates a specific capacity exceeding 135 mA h g⁻¹ during the initial cycles at low C/10 and the capacity retention while increasing the current regime is
definitively remarkable: specific capacity values of about 131, 125 and 118 mA h g$^{-1}$ are obtained at C/5, C/2 and 1C rates, respectively, that is almost 88% capacity retention from C/10 to 1C after about 80 complete cycles. The results are clearly at the level of the performances obtained with the same LiFePO$_4$-based cathode in standard liquid electrolyte cell, thus accounting for the remarkable characteristics of the newly elaborated Al-BTC MOF-laden PEO-based electrolyte.

The cell demonstrates a stable behaviour at each of the tested currents and can deliver specific capacity approaching 100 mA h g$^{-1}$ after 100 cycles at reasonably high 2C rate. In addition, the Coulombic efficiency rapidly increases to above 98% after the first cycles and remained highly stable throughout the cycles (even approaching 100% at high current regimes), indicating good mechanical stability of the electrode during the Li$^+$ ions intercalation/deintercalation process, good interfacial contact and charge transport between electrodes and polymer electrolyte and excellent reversible cycling after the initial surface reactions are complete. The cell is still able to operate at a specific capacity of 40 mA h g$^{-1}$ even at 5C rate; which accounts for the remarkable characteristics of the all solid electrolyte which facilitates the fast lithium ion exchange between the electrodes trough the polymer matrix. Finally, it is important to note that the system behaviour remains correct after prolonged cycling at high regimes, with no abnormal drift: in fact, reducing the rate to 1C almost completely restores the specific capacity (< 5% decay when comparing the specific capacity values of cycle 70 and 150 at the same 1C rate).

After the initial 160 cycles at fixed 70 °C and different C-rates were completed, the positive electrochemical characteristics of fully-solid lithium cell comprising the newly elaborated CPE upon reversible reaction with lithium were confirmed by prolonging the charge/discharge test for very long-term cycling (from 160 to 500 cycles),
by fixing the same 1C rate and modulating the temperature. The results are shown in Fig. 6.18c. The specific capacity of the cell is significantly reduced when reducing the temperature, as for the decrease in the ionic conductivity of the composite polymer electrolyte. Nonetheless, a stable cycling profile is achieved even at 50 ºC, with a reversible specific capacity of about 45 mA h g\(^{-1}\), which has never been reported so far for an all solid-state lithium polymer cell composed of Li/CPE/LiFePO\(_4\). After restoring the temperature back to 70 ºC, the decay in specific capacity of the cell is found to be limited (around 12% decay when comparing the specific capacity values of cycle 250 and 450 at the same 70 ºC) and the cell is able to operate at its initial capacity even after 500 cycles, with a slight decrease in Coulombic efficiency. Overall, the highly stable cycling performance with good capacity retention proves that the novel nanocomposite polymer electrolyte PEO+LiTFSI+Al-MOF can be a good candidate for all solid state lithium batteries conceived for moderate temperature applications.

6.4. Conclusions

In conclusion, we presented here the successful dispersion of an aluminium-based metal-organic framework (Al-BTC MOF) in a PEO-based polymer matrix, thus producing high performing polymer electrolytes for Li -based batteries. For the first time, ionic conductivity of composite polymer electrolyte (CPE) comprising poly (ethylene oxide) (PEO) and lithium bis (trifluoromethane sulfonylimide) LiN(CF\(_3\)SO\(_2\))\(_2\) (LiTFSI) has been enhanced to two order magnitude by the incorporation of aluminum based metal organic frame work (MOF) in the polymeric matrix at 20 ºC. The prepared membrane is also stable towards lithium metal even after a prolonged storage time. An excellent cycling profile was achieved, stable even at 50 ºC, with an all solid state lithium polymer cell composed of Li/CPE/LiFePO\(_4\).
References


