In this study, an ionic liquid incorporated modified MOF was synthesized to serve as an efficient electrolyte system for Li-ion batteries. Further, the MOF (IL) was doped with a lithium salt, lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) by a modified procedure. Samples with varying amount of MOF (IL) in ionic liquid were prepared, characterized and evaluated for their electrochemical behavior. A high conductivity in order of $10^{-2} - 10^{-3} \text{S cm}^{-1}$ at $51^\circ \text{C}$ and a low activation energy of ion transport was observed in all samples. The systems showed high electrochemical stability to be employed as gel electrolyte in Li ion secondary batteries. These systems showed highly reversible capacity of over 3000 mAhg$^{-1}$ in the charge-discharge studies carried out after fabricating anodic half-cell composed of Si/electrolyte/Li. These results illustrate the feasibility of the prepared modified MOF (IL) as potential solid state electrolytes for Li ion secondary batteries.

In the present work, dimensionally and morphologically controlled MOFs in electrochemical energy storage devices especially, Li-ion batteries. Very recently H. Kitagawa et al.26 studied lithium ion diffusion in MOFs in electrochemical energy storage devices especially, Li-ion batteries.

In the present work, dimensionally and morphologically controlled Metal Organic Frameworks (MOFs)1 or coordination polymers are of extreme interest due to several unique features and their applications in the fields of gas storage,2,3 separation,4 catalysis5,6 and sensors7 have been studied extensively as ionic conductors.8–12 Apart from these properties, an extraordinary feature of MOFs which makes them more interesting is that the supramolecular design of MOFs allows easy tunability depending upon the organic ligands and metal centers giving a versatile desirable properties in synthesized matrices. Recently many studies have been conducted for the application of MOFs in electrochemical energy storage devices especially, Li-ion batteries.

C. Yuan et al.13 reported that the use of nano sized particles of MOF with Lewis acidic surface are of special interests to increase ionic conductivity. These porous fillers with large surface-to-volume ratio are more helpful to stabilize the electrolyte/Li interface. B. M. Wiers et al.11 synthesized a solid lithium electrolyte by the addition of lithium isopropoxide (LiOPr) to a Mg$_2$(dodbc) (dodbc$^4-$ = 1,4-dioxido-2,5-benzenedicarboxylate) MOFs with open metal sites. The resulting electrolyte showed enhanced ionic conductivity of $3.1 \times 10^{-4} \text{Scm}^{-1}$ at 300 K. C. Gerbaldi et al.14 synthesized a poly(ethylene oxide)-based nanocomposite polymeric electrolyte (NCPE), prepared by the incorporation of specific amounts of aluminum(III)-1,3,5-benzenetricarboxylate(Al-BTC) MOFs as filler for all-solid-state Li$^+$ to improve the ionic conductivity.

Simultaneously, ionic liquids have also gained significant attention in the fields of catalysis,15,16 extraction,17,18 electrochemistry19 and chemical reactions as green solvents20,21 owing to their exclusive properties such as high solubility, non-volatility, non-flammability, wide electrochemical window and high thermal stability.22 Ionic liquid due to their inflammable property and designability allows many possibilities for new MOFs. Ionic liquid incorporated MOFs have been studied widely in the fields of catalysis23,24 and gas adsorbents.25 Very recently H. Kitagawa et al.26 studied lithium ion diffusion in ionic liquid incorporated MOFs. In these studies, ionic conductivity and Li ion diffusion was looked upon.

However, till date there are no reports on charge discharge behavior of lithium ion secondary batteries fabricated using such electrolytes. In the present work, dimensionally and morphologically controlled MOFs was carefully used to ease the ion transport in the electrolyte system. The obtained MOF based solid ion-gel electrolyte enabled efficient charge-discharge behavior with maximum discharging capacity of over 3000 mAhg$^{-1}$ with a Si anode.

**Experimental**

1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (AMImTFSI) was synthesized according to the literature.27 MOF (IL) was synthesized with a modification in an already reported electrochemical method28 and with an introduction of different ionic liquid. Dimethylformamide (DMF) and tetrahydrofururan (THF) was purchased from WAKO Co. Ltd. and used as received. Chloroform, for washing the product, was purchased from WAKO Co. Ltd. Scanning Electron Microscopy (SEM) analysis was done on a Hitachi S-4500. X-ray diffraction data was collected using Rigaku SmartLab (Rigaku, Japan) operating at 40 kV, 30 mA at a rate of 1$^\circ$ min$^{-1}$, using Cu K$\alpha$ radiation. Ionic conductivity was measured with a complex-impedance gain phase analyzer (Solartron model 1260; Schlumberger, Germany) under the frequency range from 0.1 Hz to 1 MHz. DC current measurements were carried out on ECstat-100 (EC-FRONTIER Co. Ltd., Japan). Linear sweep voltammetry measurements were carried out on Biologic VSP s/n 1190. IR spectra were recorded on a Perkin Elmer Spectrum 100.

For charge-discharge studies, silicon based anodic half-cell was prepared using CR2025 type coin cells with silicon as the working electrode ($\phi$15 mm, Kindly donated by NISSAN Co.), lithium metal as the counter electrode ($\phi$15 mm, Honjo metals, Japan) and a disc shaped polypropylene based membrane (Celgard) as separator (16 mm). The prepared silicon based anodic half-cell was charged and discharged in a galvanostatic mode with a cut off potentials limit (2.1 V to 0.03 V) at a current rate of 0.1 C (0.0172 mA) using compact charge and discharge system of EC Frontier; ECAD-1000.

**Synthesis of MOF/ionic liquid matrix by electrochemical method**25—Synthesis of the MOF (AMImTFSI) was achieved by a constant dissolution of Zn$^{2+}$ ion from Zn anode (Scheme 1). The dissolution was carried out by applying a constant direct current (DC) of 150 mA. A titanium electrode was employed as cathode. The electrolyte used in this procedure was a solution containing terephthalic acid (0.5 g, 0.003 moles), zinc nitrate hexahydrate (0.65 g, 0.002 moles) and (1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide) AMImTFSI (4.6 g, 0.011 moles) in anhydrous DMF with THF (1:1 v/v).
in DMF (50 mL). The electrochemical galvanostatic procedure was carried out for 4 hours. A white powder formed during the procedure, was filtered and washed with DMF first and then with chloroform. The sample was then dried in oven at 80°C under vacuum to afford pure MOF (AMImTFSI) or MOF (IL).

Lithium salt doping in MOF/ionic liquid matrix by grafting method—Synthesized MOF (IL) sample was activated at 120°C under vacuum for 24 hours, and the activated MOF (IL) was then soaked in 1.0 M solution of Li-TFSI in THF for 3 days at 80°C. After treating Li-TFSI (THF) for three days, the sample was washed three times with 20 mL of fresh THF by centrifugation. The sample was then kept for overnight activation under vacuum at 120°C to obtain lithium incorporated MOF (IL).

Characterization.—The synthesized AMImCl prepared according to the literature was characterized using 400 MHz nuclear magnetic resonance (NMR) spectrometer (Bruker) by 1H NMR in DMSO. Anion exchange of AMImCl was carried out with LiTFSI leading to the formation of AMImTFSI. Silver nitrate test was performed to determine the completion of successful ion exchange.

The MOF (IL) matrix, obtained as white crystalline material was characterized by XRD, FTIR, and SEM and was then subjected to electrochemical measurements for further analysis. X-ray diffractograms were shown in Fig. 1. XRD pattern of the ionic liquid modified MOF-5 is different from the conventional MOF-5. However, the Metal Organic Frameworks are very flexible and can change their structure to great extent on solvent removal. Similarly, in the present studies too, the XRD pattern of as-synthesized (blue) MOF (IL) is in good agreement with peaks observed in case of pure MOF-5 (red). But when the sample is washed and dried, the peaks shift toward larger angles. When the solvent is removed in case of MOF (IL), the side chains interact strongly, leading to the complete contraction of MOF (IL). The FT-IR spectra in Fig. 2 confirmed the formation of matrix, well resembling that of MOF-5. The peak present at 1665 cm⁻¹ in the IR spectra indicates the shift in the peak position for the carboxylate group of BDC (1,4 benzenedicarboxylate) linker from 1610 cm⁻¹, due to interaction with the Zn₄O clusters, showing the presence of bonding between organic linker and metal species. The deprotonated carboxylic acid linker bonded to the MOF-5 metal center is also indicated by the peak at 1436 cm⁻¹. These two peaks suggest that there is a bonding indicative of MOF-5. The peaks at 1505 cm⁻¹ and 1597 cm⁻¹ were indicative of the asymmetric stretching vibrations and the peak at 1388 cm⁻¹ due to the symmetrical stretching vibration of the carboxylic acid groups in BDC. Peaks in the range of 1284–730 cm⁻¹ can be attributed to the in-plane vibration of the BDC group. The two peaks in the range of 740–830 cm⁻¹ are due to CH=CH aromatic plane bends, which show that the phenyl ring was 1,4-substituted. And the new peak in the spectrum of MOF (IL) at around 1322 cm⁻¹ can be attributed to C-N stretch confirming the presence of ionic liquid in MOF matrix.

Morphological characterization of synthesized MOF (IL) was done by SEM. Fig. 3 shows a SEM image of MOF (IL) synthesized by electrochemical method showing a specific flower shaped geometry. This indicated that the morphology of MOFs depends both on the synthetic methods and ionic liquid system used as template.

Results and Discussion

Ionic conductivity.—Three samples with different weight % of 2 in AMImTFSI were prepared and ionic conductivity measurements were performed by AC impedance method. As mentioned in Experimental section, it should be noted that lithium salt was incorporated into MOF (IL), and the resulting MOF (IL) was used after washing with THF. Hence, the present system (2/AMImTFSI) does not require an external addition of Li salt. The temperature dependence of ionic conductivity for different electrolyte compositions of 2 in
AMImTFSI are shown in Fig. 4a. Arrhenius plots showed linear profiles with rise in temperature, indicating no decomposition or phase change over the temperature range. As expected the ionic conductivity decreased with increase in wt% of 2 in AMImTFSI because of the change in physical state from liquid to gel (soft solid). The ionic conductivities of the samples were calculated and were in the order of $10^{-2} \sim 10^{-3} \text{ S cm}^{-1}$. The sample in liquid state with 10 wt% of 2 in AMImTFSI showed slightly higher ionic conductivity i.e. $1.0 \times 10^{-2} \text{ S cm}^{-1}$ at 51°C. And the high ionic conductivity of the solidified ion-gel electrolyte is because of higher possibility of long distance migration under dimensionally controlled ion conductive path rather than in fully amorphous random-walk system. Though other coordination polymers also show ordered structure and regulation in ion conductive path, here ionic liquids itself will act as ion carrier. So the synergistic effect of ordered structure and the presence of ionic liquid as the solvent for ion conduction, led to the high ionic conductivity which is also evident from the low values of activation energy.

The solidified ion-gel electrolyte system showed comparable ionic conductivity in the range of $10^{-2} - 10^{-3} \text{ S cm}^{-1}$ with other MOF

Figure 2. Infrared spectra of MOF-5 and MOF (IL) 1.

Figure 3. SEM images of MOF (IL) 1 showing flower shaped morphology.

Figure 4. (a) Arrhenius and (b) VFT plots for different compositions of MOF (IL) in AMImTFSI.
Table I. VFT parameters for different compositions of 2 in AMImTFSI.

| State   | Sample in AMImTFSI | A (Scm\(^{-1}\)K\(^{1/2}\)) | B (K)    | R\(^2\) | \(\sigma\) at 324K (Scm\(^{-1}\)) |
|---------|--------------------|-----------------------------|----------|---------|-----------------------------|
| Liquid  | 10 wt% MOF (IL)    | 11.21                       | 722.4    | 0.999   | \(1.0 \times 10^{-2}\)      |
| Liquid  | 20 wt% MOF (IL)    | 3.99                        | 662.2    | 0.998   | \(5.0 \times 10^{-3}\)      |
| Gel     | 30 wt% MOF (IL)    | 1.88                        | 636.5    | 0.998   | \(2.3 \times 10^{-3}\)      |

Figure 5. DC Polarization profiles for Li/electrolyte/Li cell with different wt% of MOF-5 (IL) 2 in AMImTFSI.

DC polarization measurements.—Chronoamperometry experiments for all the three samples were done to study the steady state current and Li ion diffusion in MOF (IL) matrices. A DC voltage of 0.03 V was applied across the Li/electrolyte/Li type cell for an indefinite period of time until the current reached a steady state. As shown in Fig. 5 the steady state current flowing was contributed only by Li ion conduction which shows that Li salt was successfully incorporated into the MOF (IL) matrices.

All these experiments were done in a glove box filled with argon gas with very low moisture content.

Linear sweep voltammetry scan (LSV).—Electrochemical window of the synthesized electrolytes with different compositions of 2 in AMImTFSI was determined by LSV in Li/electrolyte/Pt cell configuration at a scan rate of 10 mV s\(^{-1}\) within 0 to 6 V range of potential. LSV curves obtained for different compositions are shown in Fig. 6a. For all the samples, a potential working window of 5.22 to 5.55 V was obtained. After 5.22 V / 5.55 V, sudden increase in the current exhibited the occurrence of an electrochemical reaction. To observe lithium plating and stripping processes, Fig. 6b shows cyclic voltammetry experiment performed for 20 wt% of 2 in AMImTFSI at a scan rate of 10 mV s\(^{-1}\) in Li/electrolyte/Li cell. Almost ideally reversible peaks for both lithium stripping and lithium plating processes were observed.

This indicated that the MOF (IL) matrices possess high electrochemical stability and are able to appease the requirement of high voltage lithium ion batteries.

Figure 6. (a) LSV curves of Li/electrolyte/Pt cells with different electrolyte compositions. (b) Cyclic Voltammogram of Li/electrolyte/Li cells with 20 wt% of 2 in AMImTFSI electrolyte composition.
Fig. 7b shows the cycling performance of Li/electrolyte/Si cell fabricated using 30 wt\% MOF (IL) in AMImTFSI with 30 \(\mu\)L of EC:DEC = 1:1 for 10 cycles. (b) Rate cycling performance of Li/electrolyte/Si cell fabricated using 30 wt\% MOF (IL) in AMImTFSI with 30 \(\mu\)L of EC:DEC = 1:1 for 40 cycles.

**Charge-discharge characteristics.**—The charge-discharge characteristics were studied for the 30 wt\% of 2 in AMImTFSI electrolyte composition in a coin anodic half-cell configuration using Si anode (theoretical capacity: 4200 mAh g\(^{-1}\)) with 30 \(\mu\)L of EC: DC = 1:1 at a current rate of 0.1C (0.0172 mA) (Fig. 7). The 30 \(\mu\)L of EC:DEC was added to the electrolyte composition during the cell fabrication just to wet the electrode surface. The EC:DEC also allows quick formation of solid electrolyte interface. The 30 wt\% of 2 in AMImTFSI was a gel state product compared to other two compositions (liquid), therefore the charge discharge behavior of this particular electrolyte composition was studied extensively. Although the other electrolytes have better electrochemical parameters, the objective of the study to arrive at a gel state electrolyte was the motivation behind the choice of this electrolyte.

The result of charge-discharge of 30 wt\% of 2 in AMImTFSI at 0.1 C for 10 cycles is shown in Fig. 7a. The first cycle showed highly irreversible capacity because of SEI formation in the first cycle. But the capacity tends to stabilize after the first cycle which suggests the formation of stable conductive SEI layer after the first cycle. Fig. 7b shows the cycling performance of Li/electrolyte/Si cell fabricated using 30 wt\% of 2 in AMImTFSI at different rates in order to evaluate the practical use of the electrolytes in lithium ion batteries. The constructed cell with 30 wt\% of 2 in AMImTFSI exhibited a stable cycling behavior and showed reversible discharge capacity of 3000 mAh g\(^{-1}\). Coulombic efficiency of the cell was observed to be around 90\% which indicated few electrochemical reaction was occurring resulting in the decomposition of the electrolyte material. The initial fluctuation in Coulombic Efficiency before 20 cycles can be attributed in part to the formation of a solid-electrolyte interphase (SEI). This passivation layer is expected to form through a decomposition reaction of the solvent EC:DEC and the electrolyte (till 11 cycles). And after the completion of SEI formation and subsequent stabilization of SEI (12–21 cycles), the coulombic efficiency tends to become constant or increased slightly in further cycles. As the SEI layer advances over time the negative and positive electrodes, the time dependent coulombic efficiency is expected to increase. The formation of stable SEI layer is also evident from the high capacity retention at increased current rates.

**Conclusions**

A modified MOF (IL) framework was synthesized by the electrochemical reaction resulting in a modified MOF-5 with AMImTFSI. The obtained crystalline product was characterized by XRD, FT-IR, SEM and TEM analysis. XRD analysis showed the crystallinity of the MOF in ionic liquid matrix. The FT-IR spectrum of modified MOF (IL) \(^1\) showed close resemblance with MOF structure. SEM and TEM showed the change in morphology from conventional cubic to more porous distinct flower shaped morphology because of the incorporation of highly conducting AMImTFSI liquid.

The electrochemical analysis of the sample was done by doping the electrolyte with lithium salt by the modified procedure. After incorporation of Li-salt in MOF (IL) \(^1\) samples with different wt\%, results MOF (IL) matrices showed the highest ionic conductivity for 10 wt\% MOF (IL) in AMImTFSI. The DC polarization measurements showed the successful incorporation of lithium in MOF (IL) matrix. The compound showed an electrochemical window of 5.22–5.55 V. After fabricating Si/electrolyte/Li type half cell, 90\% coulombic efficiency was observed in the presence of 30 \(\mu\)L of EC: DC = 1:1.

Thus, we conclude that the modified MOF with ionic liquid framework prepared in ionic liquid system by electrochemical method revealed high ionic conductivity as a solidified ion-gel electrolyte and wide electrochemical window. Further when Li/electrolyte/Si type anodic half cell was fabricated the cell exhibited a reversible capacity of 3000–3300 mAh g\(^{-1}\). These enhanced attributes attained from new MOFs affirm that the prepared modified MOF (IL) to be a prospective electrolyte in energy storage devices.

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