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# Development of ion conducting polymer gel electrolyte membranes based on polymer poly(vinylidene fluoride-co-hexafluoropropylene), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide) ionic liquid and Li-salt with improved electrical, thermal and structural properties

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## Thermo Gravimetric Analysis (TGA):

The TGA and first derivative of TGA (DTGA) plots of the pure PVdF-HFP, Pure IL, BMIMTFSI, polymer gel electrolyte membranes, PVdF-HFP+x wt.% BMIMTFSI (where x= 20, 40, 60 and 80) are shown in Figure S1 and the TGA and first derivative of TGA (DTGA) plots of the (PVdF-HFP+20% LiTFSI)+x wt.% BMIMTFSI (where x=0, 20, 40, 60 and 70) are shown in Figure S2 (high thermal stability (~300-350°C) of all the prepared polymer gel electrolyte membranes is confirmed). PVdF-HFP and IL, BMIMTFSI are decomposed in a single step respectively at ~475°C and ~465°C (see Figure S1 (a) and (b)). However, the PVdF-HFP + IL gel membranes exhibit two step decomposition mechanisms as shown in Figure S1. It is very difficult to distinguish the decomposition temperature of polymer and IL alone at lower content of added IL (say at 20 wt % and 40 wt.%). However, on increasing the IL content (60 and 80 wt%) in PVdF-HFP+IL gel membrane, two decomposition peaks (marked as x and y) are observed (see Figure S1 (e) and S1 (f)) which are respectively related to the decomposition temperature of complex formed (i.e. between IL and polymer) and the decomposition temperature of polymer.

Now, from Figure S2 (a), it can be seen that the polymer electrolyte i.e. PVdF-HFP+20 wt.% LiTFSI, exhibits three step decomposition mechanism with decomposition peaks (marked as $P_1$, $P_2$ and $P_3$) at ~468 °C (decomposition temperature of polymer, PVdF-HFP), 340°C (related to the decomposition temperature of complex formed between polymer with cation of Li-salt) and 310°C (decomposition temperature of the LiTFSI salt) (see Figure S2 (a)). From Figure S2 (a), it can be seen that, the decomposition peak at ~340°C (which may be related to the decomposition temperature of complex formed between polymer, PVdF-HFP with cation Li-salt) is very small as compared to the other peaks. Again, when we add different amounts of IL in polymer electrolyte (i.e. PVdF-HFP+20 wt.% LiTFSI), we get similar three decomposition peaks (marked as $P_1$, $P_2$ and $P_3$) at ~424 °C (decomposition temperature of polymer,PVdF-HFP), 314 °C (related to the decomposition temperature of complex formed between polymer and Li- salt) and 300°C (decomposition temperature of LiTFSI salt) (see Figure S2 (a)) but at somewhat lower temperature. This can be concluded as, at lower amounts of added IL (20 wt.%) in polymer electrolyte, the thermal stability decreases by a small amount but these are still suitable for practical application. Further, on increasing the amount of added IL in the polymer electrolyte, the intensity of the peak related to the decomposition of the polymer-salt complex ($P_2$) starts decreasing and is almost disappeared at higher concentration of added IL in the system (see Figure S2 (b-e)). The thermal stability of the prepared membranes also increased with increasing IL content and reached upto ~460°C for higher concentration (~70wt.%) of the added IL in the polymer gel electrolyte membranes. The overall conclusion of the above discussion is that, when IL was present in small amount in polymer electrolyte, some amount of LiTFSI salt gets complexed with the polymer backbone but when we increase the amount of the IL in polymer electrolyte it reduces the complexing ability of salt with polymer. It may be due to the presence of IL which reduces the complexing ability of Li-salt with polymer and because of LiTFSI salt, which has low lattice energy and also a low tendency to form ion-pairs and complex as discussed earlier. Therefore, On the basis of above discussions we can conclude that in the present study, IL BMIMTFSI and LiTFSI salt both provide more free ions to the polymer gel electrolyte membranes which plays a significant role to enhance the overall ionic conductivity of the system. To account for this, complex formation between cations of Li-salt and the IL with polymer cannot be excluded and spectroscopic studies are give in the following section to confirm this hypothesis.

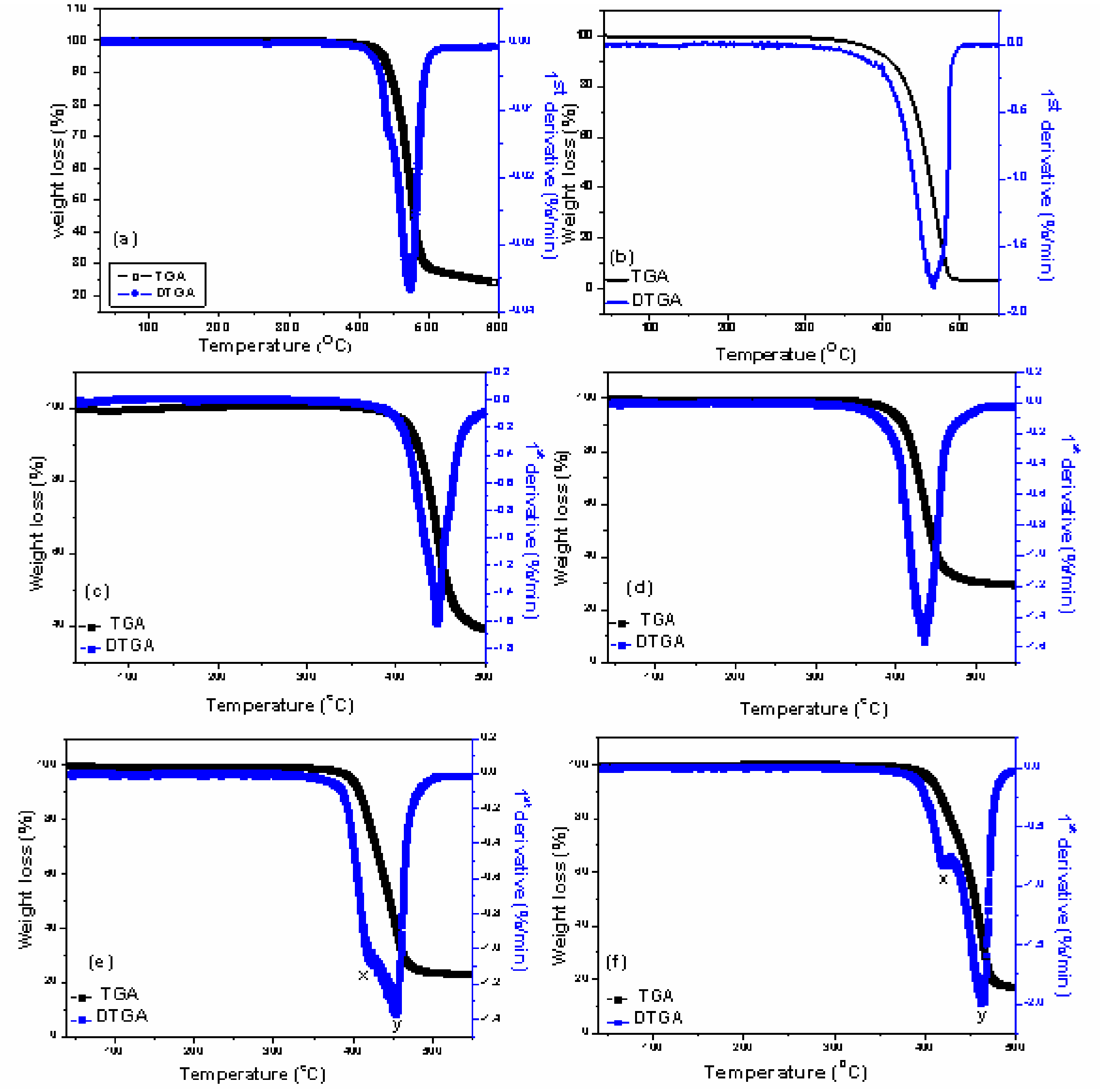

**Figure S1**: TGA and DTGA curves for (a) pure PVdF-HFP, (b) pure IL, and PVdF-HFP +x wt % IL gel membrane for (c) x= 20, (d) x= 40, (e) x= 60 and (f) x= 80 respectively.

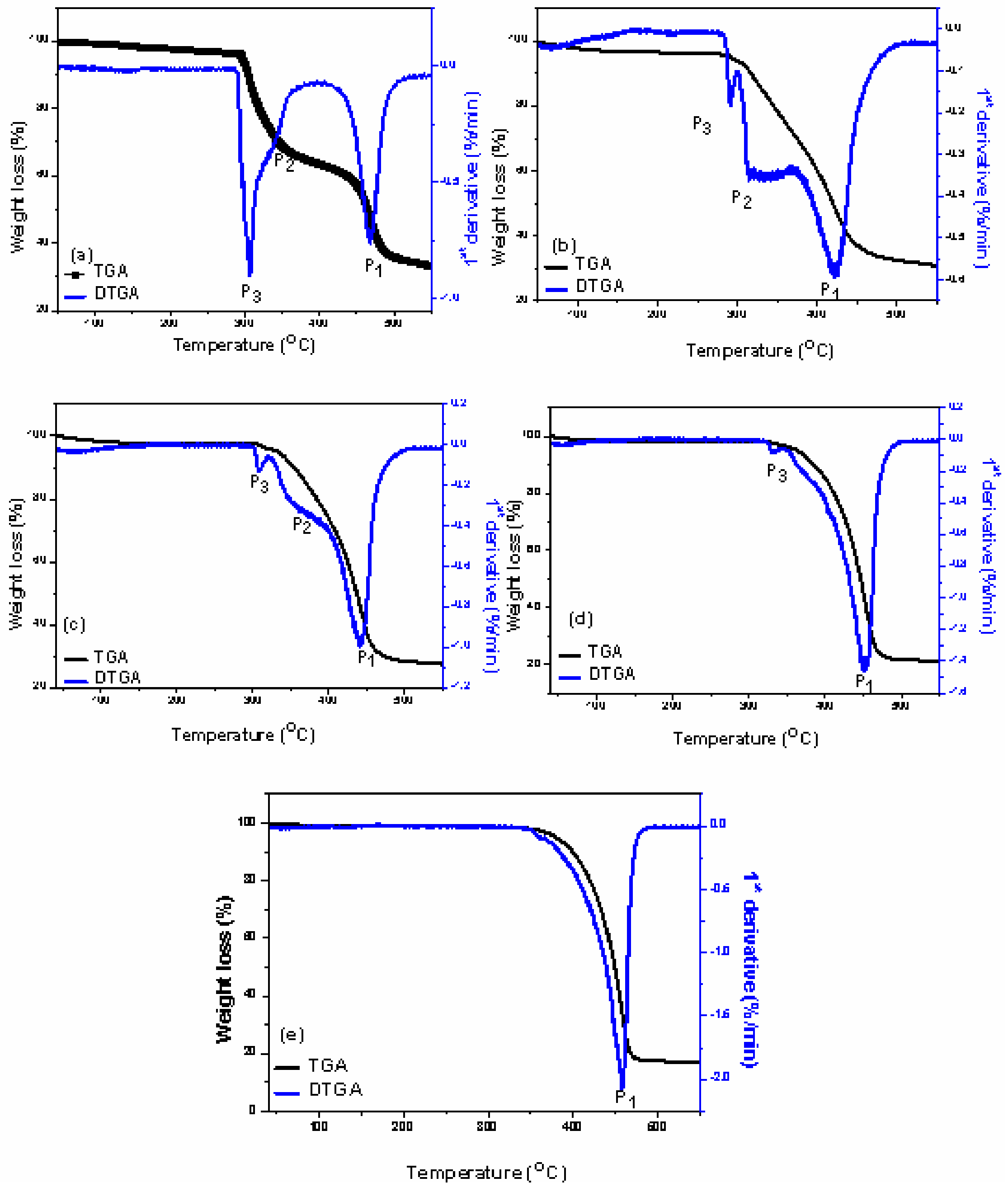

**Figure S2:** TGA and DTGA curves of PVdF-HFP +20wt % LiTFSI+x wt.%IL gel membrane for (a) x= 0, (b) x= 20, (c) x= 40, (d) x= 60 and (e) x= 70 respectively.