



Short communication

New high-throughput methods of investigating polymer electrolytes

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ABSTRACT

Polymer electrolyte films have been prepared by solution casting techniques from precursor solutions of a poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP), lithium-bis(trifluoromethane) sulfonimide (LiTFSI), and propylene carbonate (PC). Arrays of graded composition were characterised by electrochemical impedance spectroscopy (EIS), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) using high throughput techniques. Impedance analysis showed the resistance of the films as a function of LiTFSI, PC and polymer content. The ternary plot of conductivity shows an area that combines a solid-like mechanical stability with high conductivity, $1 \times 10^{-5} \text{ S cm}^{-1}$ at the composition 0.55/0.15/0.30 wt% PVdF-HFP/LiTFSI/PC, increasing with PC content. In regions with less than a 50 wt% fraction of PVdF-HFP the films were too soft to give meaningful results by this method. The DSC measurements on solvent free, salt-doped polymers show a reduced crystallinity, and high throughput XRD patterns show that non-polar crystalline phases are suppressed by the presence of LiTFSI and PC.

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1. Introduction

Ion containing polymers have been proposed as electrolytes for many solid state electrochemical devices. Over the past few decades important applications have been found in lithium batteries, supercapacitors, electrochromic windows and chemical sensors [1–4]. In all these areas there is a need to optimise the polymer composition and other aspects of the synthesis to produce the most desired combination of properties for the particular application. This is generally a very laborious task for polymers, in particular because of the large number of compositional and other variables. Previous studies have been made for poly(methyl methacrylate) [5], poly(acrylonitrile) [6,7], and poly(vinylidene co-hexafluoropropylene) (PVdF-HFP) [8–11], in which it has been found that the addition of a plasticiser (a solvent of low volatility) generally decreases the crystallinity and increases the amorphous fraction; both of these effects and the addition of a suitable salt should cause a systematic increase in the ionic conductivity. A maximum value in the conductivity/salt concentration plot is usually found in the polymer-free liquids, due to the decrease in mobility and the increase in ion-pairing at high salt content. More detailed investigations into the morphology of the polymer and its interaction with both plasticiser and lithium salts have concluded that certain phases are suppressed by adding these components [12].

High throughput (HT) techniques have been applied to polymers for the pharmaceutical industry and there are many instances of HT techniques being applied to the discovery of materials for lithium ion batteries, both negative [13,14] and positive electrode materials [15,16]. However methods of characterizing polymer electrolytes on a HT scale are much less advanced. A technique using optical dyes for measuring the thickness of polymer films was demonstrated successfully when compared to conventional measurement methods [17], and HT electrochemical impedance spectroscopy has been demonstrated on solid state gas sensing materials [18] but none relating to polymer electrolytes.

This work demonstrates the concept of applying HT techniques to screening and optimisation studies of polymer electrolytes which are immobile gels of the type suggested for use in some commercial lithium-ion-polymer cells. The essential components are an inert polymer, a plasticiser and an ionic salt dissolved in the plasticiser. Such polymers are particularly amenable to rapid fabrication of variable composition arrays because the synthesis requires only dissolution of the components in a volatile solvent that subsequently evaporates to leave a thin film similar to what is used in the device. In this work the three components were (PVdF-HFP), propylene carbonate (PC), and bis(trifluoromethane) sulfonimide lithium salt (LiTFSI).

An electrode array design previously used by us to characterise electrode materials [16], has been adapted in this work for the characterisation of the polymers using electrochemical impedance spectroscopy (EIS), X-ray diffraction (DSC) and differential scanning calorimetry (DSC) on a HT scale.

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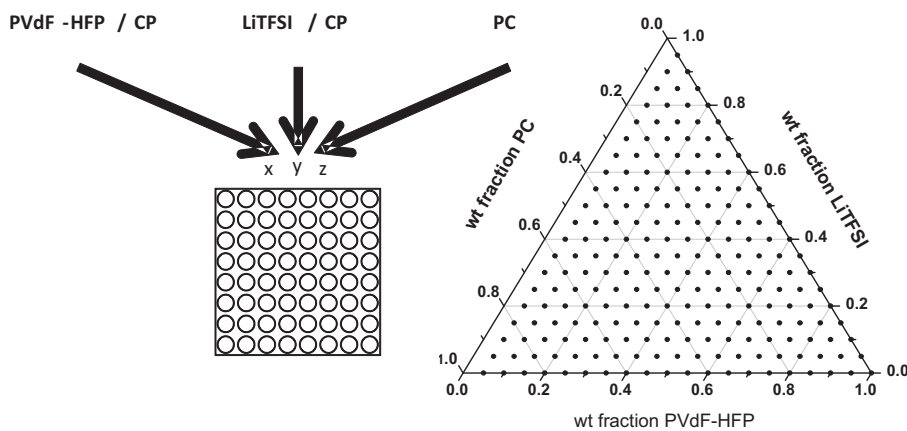


Fig. 1. Compositions of polymer films studied in this high throughput study.

2. Experimental

2.1. Sample fabrication

2.1.1. High-throughput testing

PVdF-HFP (Aldrich, av. Mn \approx 130,000, av. Mw \approx 400,000) and LiTFSI (Aldrich, puriss., \geq 99.0%) were dried under vacuum at 100 °C for 12 h prior to use. Propylene carbonate anhydrous (PC) (Aldrich, 99.7%) was used as received as the plasticiser, it was handled carefully within a glove box at all times to ensure no water impurities. The cyclopentanone (CP), (Aldrich, 99+%) was distilled prior to use to remove any water and then kept in the glove box. All further procedures were undertaken inside an argon filled glove box until the samples were placed in a hermetically sealed cell for the impedance measurements. Appropriate weights of PVdF-HFP, PC and LiTFSI (Aldrich, puriss., \geq 99.0%) were dissolved in the co-solvent CP to give standard stock solutions around 10% by mass. The solutions were metered into 8 ml vials at the appropriate ratios to give solutions whose non-volatile fractions varied to cover a range of compositions shown in Fig. 1. To ensure a homogenous mixture, the vials were placed on a vortex mixer (Fisherbrand, Whirlimixer) before use.

The design of the multi-electrode cell, shown in Fig. 2, has an array of 64-electrodes of 6 mm diameter aluminium electrodes supported on sprung contacts similar to that described before [16]. The polymer samples were deposited on the electrode array as described below and were contacted by a 1.5 mm thick upper elec-

trode made of carbon loaded rubber with a conductance better than 1 S cm^{-2} (RS components C5-9134 carbon loaded conductive silicone). A stainless steel current collector was positioned above this and sprung contacts provided pressure from above and an electrical path to the connector in the lid. The thickness of each electrode was measured with a micrometer with tolerance values of $1 \pm 5 \mu\text{m}$, before any deposition of the electrolyte and again after the experiment had taken place.

The conductivity of 64 different compositions shown in Fig. 1 was measured with 8 arrays, each containing 8 compositions repeated on 8 electrodes. For each sample a 25 μl volume was measured in a pipette and placed on top of an electrode ensuring an even coverage across the entire electrode area. The co-solvent was evaporated off by leaving the cell in the glove box at room temperature. Mass measurements indicated that removal of CP took 1.5 h at 25 °C; after this time thickness measurements using a micrometer were made before transferring into the hermetically sealed measurement cell. The sample thicknesses varied $\pm 5\%$ around 100 μm , corresponding to densities around 1.4 g cm^{-3} .

2.1.2. Conventional testing

The same method for preparing films was taken for the conventional testing method. Films with compositions of 0.5, 0.45, 0.05 and 0.5, 0.4, 0.1 of PVdF-HFP, PC and LiTFSI respectively were prepared. Appropriate weights of PVdF-HFP, PC and LiTFSI (Aldrich, puriss., \geq 99.0%) were dissolved in the co-solvent CP to give standard stock solutions around 10% by mass, 0.6 ml of these solutions was

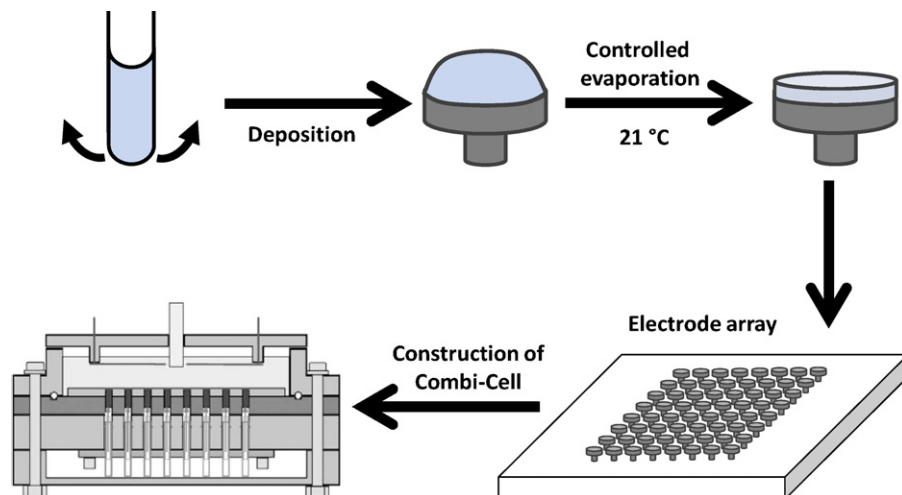


Fig. 2. Schematic diagram showing the sample deposition method and a cell design taken from previous work [16].

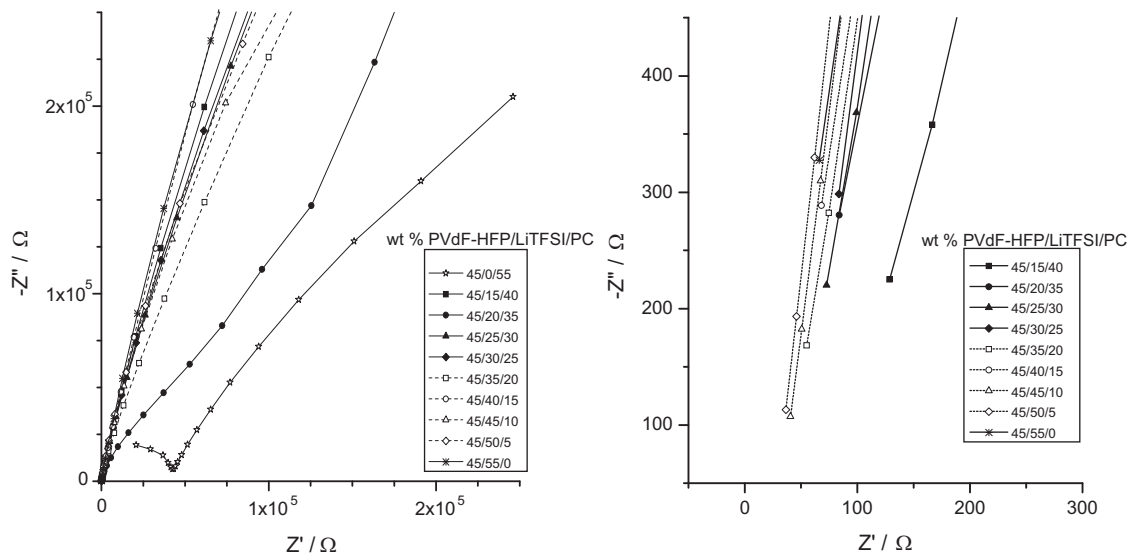


Fig. 3. Complex impedance Nyquist plots at low and high resolution for 9 polymer samples of different compositions.

then deposited onto glass slides. The co-solvent was then removed as described above; this resulted in the formation of mechanically robust free standing films of around 100 μm thickness. These films were then sandwiched between two 1 cm diameter stainless steel discs and the impedance measurements were recorded using the same settings as for the combinatorial method.

2.2. Sample characterisation

2.2.1. Impedance spectroscopy

Ionic conductivity was measured using the complex impedance technique with a Solartron SI 1287 electrochemical interface coupled with a Solartron 1250 frequency response analyser over the frequency range of 0.1 Hz to 65 kHz.

Analysis of the results in Z-view (Scribner Associates) showed that for most cases the frequency dispersion could be fitted to a constant phase element and resistance representing the imperfectly blocking electrodes in series with a high frequency real axis intercept indicating the electrolyte resistance as obtained by Jiang et al. [11]. The conductivity (σ) of the polymer electrolytes at each composition was estimated from the averaged electrolyte resistance (R), the electrode area (A) and the film thickness (l) using the equation $\sigma = l/AR$ and was tabled as a function of the three composition variables in Origin 8.1 to display the data as a contour map by linear interpolation.

2.2.2. Combinatorial X-ray diffraction (XRD)

Sample arrays with composition variations were prepared in the form of thick films on 6 mm diameter aluminium substrates as for the impedance measurements. X-ray diffraction patterns of the PVdF-HFP/LiTFSI/PC membranes were obtained using a high-throughput X-ray diffractometer (Bruker C2 GADDS) with a Cu $K\alpha$ radiation as source over the 2θ range 15–46°. The sample positions on the multielectrode array plate were programmed into the diffractometer allowing central measurements of each sample to be taken automatically. The scan time was 5 min per sample, with diffraction patterns of the whole array being completed within 6 h.

2.2.3. Differential scanning calorimetry (DSC)

The same arrays as above were used for high throughput DSC using a Mettler model DSC20 oven connected to a Mettler TA4000 controller. Samples were heated at 10° per minute from room temperature to 200 °C and then cooled to –150 °C at the same rate. This

cycle was repeated once more with both cycles being performed at 10 °C min^{-1} .

3. Results and discussion

3.1. Impedance and conductivity

Fig. 3a illustrates a typical set of impedance plots for one batch of samples. It can be seen that the sample containing no lithium salt exhibits a high frequency semi-circle characteristic of the sample resistance in parallel with its dielectric capacitance. In the other samples, which contained varying degrees of LiTFSI, the semicircles were absent, indicating that the sample resistances (real part) were much lower than the dielectric impedance (imaginary part) within the frequency range measured. This interpretation was confirmed by equivalent circuit fitting as described in Section 2.2.1 above with the sample resistance placed in series with a constant phase element (CPE) representing partially blocking behaviour of the blocking electrodes due to surface roughness and possible faradaic reactions. For the more conductive samples, as seen in Fig. 3b, the impedance plot is rescaled to show the sample resistances at the x-axis intercepts, systematically decreasing towards the origin as the amount of LiTFSI was increased across the series.

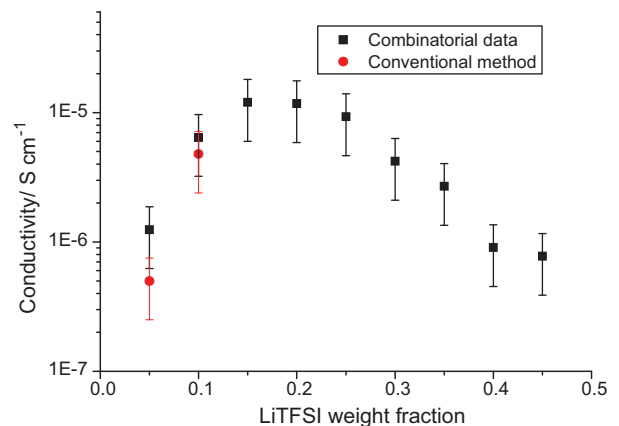


Fig. 4. Conductivity vs. salt mass fraction for 0.5 mass fraction of PVdF-HFP with error bars to indicate standard deviations.

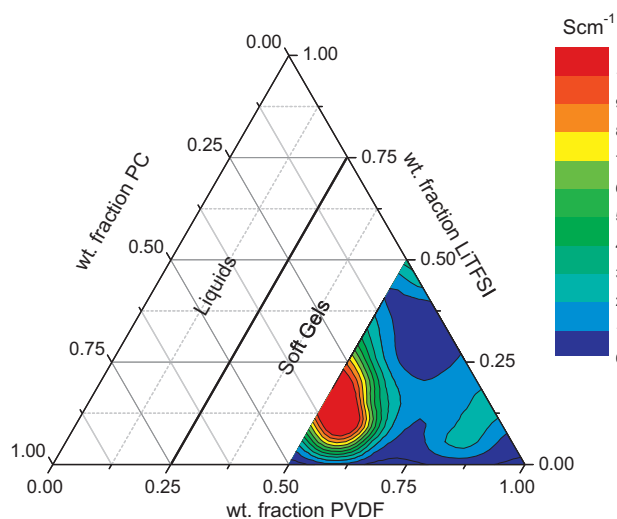


Fig. 5. A contour map of the conductivity vs. composition, indicating the region where the mechanical properties were acceptable and showing the “hot spot” for the optimum combination of conductive and mechanical properties.

Fig. 4 shows the effect of the plasticiser/salt ratio for a polymer mass fraction of 0.5. It shows an initial steep rise in conductivity at low salt content followed by a plateau then a slow decline above a LiTFSI mass fraction of 0.25. The errors are assumed to be mainly due to uncertainties in the sample thicknesses and cross sectional areas, and are reflected in the irregularities in an otherwise smooth variation of $\log \sigma$ with composition as displayed in **Fig. 4**. We would stress our belief that such errors are not inherent the HT technique itself, which would benefit greatly from better cell design and control of sample geometry, which were beyond the scope of this study whose aim was a simple demonstration of concept. Also shown for comparison are two measurements obtained through our conventional approach and are seen to be in good agreement with the combinatorial data.

Fig. 5 shows the region of solid-like behaviour and the corresponding conductivity contour map as determined for the region. Regions of the composition diagram beyond a PC mass fraction of 0.5 were deemed to be unsuitable for measurement or use as polymer membranes. Although the “soft gels” formed free standing films, they suffered from liquid release or “sweating” under pressure, a problem that has been noted in the case of methylpyrrolidinium-TFSI in PVdF-HFP, [19]

The conductivity results showed trends in composition that were generally in accordance with those found by Jiang et al. using conventional methods, i.e. the conductivity decreased at high polymer content due to the viscosity increase. A peak conductive area ($\sim 10^{-5} \text{ S cm}^{-1}$) can be seen for compositions around 55% PVdF-HFP, 15% LiTFSI and 30% PC that were not studied in the previous work. The value of the high throughput technique is seen in the detail of the mapping compared with previous studies based on fewer different compositions [11].

3.2. High throughput X-ray diffraction

The diffraction patterns of some polymer films with differing amounts of salt and plasticiser are seen in **Fig. 6**. The pure PVdF-HFP sample shows three distinct peaks at 18, 20 and 26.6° corresponding to non-polar, polar and nonpolar phases respectively. With the addition of LiTFSI the nonpolar phases at $2\theta = 18.2$ and 26.6° disappear whereas the polar phase at $2\theta = 20^\circ$ survives, with a broadening of the peak. This destabilisation of nonpolar phases presumably in favour of an amorphous phase is further evidence

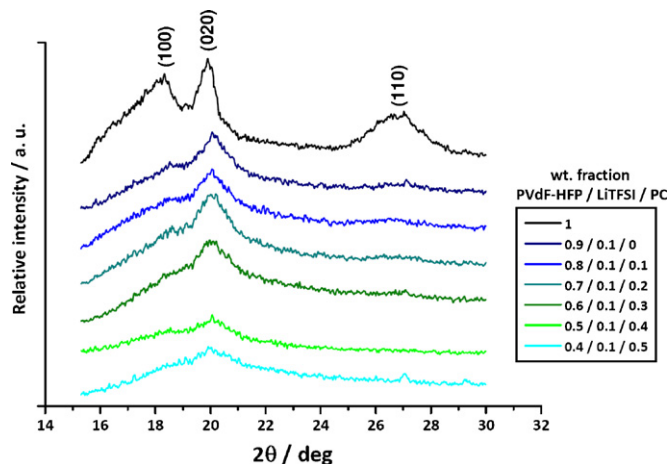


Fig. 6. X-ray diffraction patterns of pure PVdF-HFP and different mass fractions of LiTFSI and PC.

for solvation of LiTFSI by PVdF, which is equivalent to plasticisation of PVdF by LiTFSI. A strong plasticising effect of LiTFSI has also been noted previously in poly(oxyethylene), with unusually high conductivities at high salt content [20].

This effect has been noted for LiTFSI with various solvents in PVdF-HFP [12] and for ionic liquids [21]. On addition of PC the broadening continues until the crystalline peak has almost disappeared, when at this point the film has physical properties more similar to those of a gel than of a solid. This is consistent with the assumption that swelling the matrix with solvent will extend the amorphous region of the polymer [22].

3.3. Differential scanning calorimetry (DSC)

This type of thermal analysis is useful in estimating how the mechanical properties of the film will change with temperature and ultimately the suitability for the intended application. In principle, DSC can give microstructural information regarding the crystal melting points and degree of crystallinity. However, in this case solvent evaporation complicated the analysis of samples across the array, and therefore we show two solvent-free examples in **Fig. 7**, where crystallinity was most prevalent, with clean melting and crystallising peaks at 110°C and 140°C respectively and a much decreased degree of crystallinity in the salt-containing sample. These results are evidence for a plasticising interaction between the salt and polymer. Further peaks that appeared on heating the doped sample are difficult to assign without further study and therefore outside the scope of this study.

3.4. An appraisal of this high throughput technique

As mentioned above, the HT method as developed in this work introduced sources of error that would not normally be encountered in a conventional approach, but it may be expected that the error margins would be considerably reduced with refinement of the technique. Therefore the following analysis concerns the benefits of HT in this case.

First, it should be noted, that electrolytes are usually multi-component systems and therefore a full investigation requires variation of all compositional parameters, which necessitates a number of samples that increases exponentially with the number of independent composition variables. The conventional method e.g. Nekoomanesh et al. [23] typically involved a few hundred milligrams for the preparation of for a single film of each composition, then measurement of conductivity and DSC scans in individual cells.

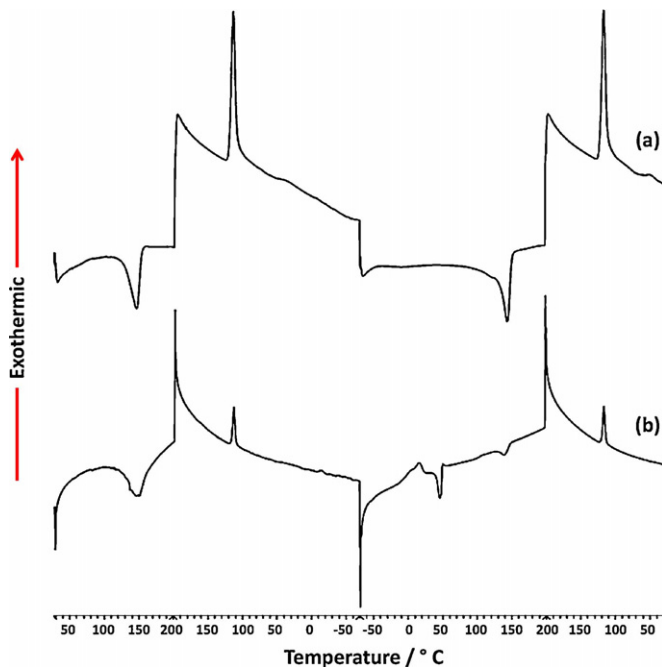


Fig. 7. DSC curves of (a) pure PVdF-HFP and (b) PVdF-HFP/LiTFSI mass fraction 0.6/0.4.

One obvious advantage of the high throughput concept is economy of sample preparation – here the solutions contained only a few tens of milligrams for each composition. This translates into valuable savings of cost and effort in the cases where the salts are expensive or even specially synthesised for evaluation. The “hot spot” at around 55% PVdF-HFP, 15% LiTFSI and 30% PC highlighted above demonstrates the importance of including a large number of samples for a successful investigation, because a coarser mesh could have missed the result.

The other advantage is the time and effort spent in construction and measurement of the cells. In the conventional example, cited above, the number of compositions was limited by the time available, which can be estimated as one day for each composition to be cycled from 20 °C to 80 °C and back. Therefore the cited study examined only five compositions, with a consequent loss in scope and resolution in composition and temperature. In the present study, all 64 electrodes were held in the same temperature-controlled array so that the time saving was effectively 64 on a per-sample basis. Other time savings could undoubtedly arise from automated mixing and dispensation of the solutions to form the arrays.

4. Conclusion

This work demonstrates the concept of HT screening of multiple samples of polymer electrolytes to find the composition ranges

where the highest ionic conductivities may be found. The application of a large soft contact was validated and shown to simplify the measurement relative to one involving two individual contacts to each sample. The rapid sequential impedance technique was found to be sufficiently accurate to measure samples across the 64-sample array in a few hours of automated testing. Coupling with HT diffraction and DSC measurements showed correlations between the conductivity trends and changes on the sample microstructures with the proportions of the additives. A peak conductive area ($\sim 10^{-5} \text{ S cm}^{-1}$) was observed for compositions around 55% PVdF-HFP, 15% LiTFSI and 30% PC where the film also had favourable mechanical properties for use as a separator in a lithium battery.

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