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The use of novel VDF–HFP–CTFE terpolymers in lithium-ion polymer cells

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Abstract

Porous polymer films and plasticised polymer films of vinylidene fluoride (VDF)–hexafluoropropylene (HFP)–chlorotrifluoroethylene (CTFE) terpolymers have been fabricated from a range of solvents. Significant 2EC/PC solvent uptake was measured at 60 °C for VDF–HFP–CTFE terpolymer films but structural integrity was maintained.

0.625 Ah soft packaged graphite—$LiCoO_2$ test cells have been fabricated containing porous VDF–HFP–CTFE terpolymer films as separator. Ninety-eight percent of Rated Capacity was measured at $2C$ rate. Four hundred and fifty-four cycles were obtained at C rate to 80% of Rated Capacity. Thin 4–5 μm plasticised VDF–HFP–CTFE terpolymer films have also been produced.

Keywords: Rechargeable lithium batteries; VDF–HFP–CTFE terpolymer

1. Introduction

There is currently much interest in the use of PVdF-based polymers in lithium-ion polymer cells [1,2]. We have found that good quality polymer films can be produced from homopolymer PVdF [3]. However, homopolymer PVdF has both a high crystallinity and a limited range of casting solvents. Previously we have reported results for modifications to the properties of homopolymer PVdF that were achieved by radiation grafting of selected monomers to the polymer [4]. Changes to the properties can also be achieved by copolymerisation of vinylidene fluoride (VDF) with monomers such as hexafluoropropylene (HFP) and chlorotrifluoroethylene (CTFE). The crystallinity can be reduced by the incorporation of HFP to produce a copolymer. Such a copolymer is also soluble in an increased range of solvents. The introduction of HFP decreases the melting point of the polymer and increases the uptake of electrolyte. The combination of these two factors could lead to a degradation of the mechanical properties of polymer film at increased temperatures. The addition of CTFE to the VDF–HFP copolymer has the effect of increasing the melting point and increasing the amorphous content. Gel electrolyte membranes containing a VDF–CTFE copolymer have been reported to have high conductivity and good compatibility with the lithium metal electrode [5].

2. Experimental

VDF–HFP–CTFE terpolymers containing a range of VDF:HFP:CTFE ratios have been produced by Solvay. These polymers have a low melt flow index which has shown to be beneficial in the fabrication of polymer films that can absorb significant quantities of electrolyte [3]. Increased polymer molecular weight also decreases the dissolution of the polymer in the plasticisers during cell operation.

Samples of polymer film for electrolyte absorption tests were produced from solutions of the polymers in dimethyl acetamide using in-house coating equipment. A series of EC/PC (2:1, w/w) absorption tests were carried out at 21, 40 and 60 °C on polymer samples of dimension 32 mm × 36 mm and of thickness 50–60 μm. A significant excess of solvent was used for these tests. Samples of homopolymer PVdF (SOLEF® 1015) and copolymer VDF–HFP (SOLEF® 21216) were also evaluated for comparison.

A much wider range of casting solvents is available for VDF–HFP–CTFE terpolymer compared to homopolymer PVdF. Plasticised VDF–HFP–CTFE terpolymer films have been produced from dimethyl carbonate. Porous VDF–HFP–CTFE terpolymer films have been produced from

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solvent/non-solvent systems [6], such as acetone/2-butanol and dimethyl formamide/1-octanol. It has been observed that the correct ratio of solvent:non-solvent and coating conditions are critical to the formation of porous films. Air permeability measurements of the porous films were made using a Model 4340 Automatic Densometer and Smoothness tester (Gurley Precision Instruments). Settings of 100 cm^3 and 1 $in.^2$ orifice were used, at standard pressure.

Test cells were fabricated by adopting either a flat-wound cell design or a folded stack cell design, using porous electrodes in conjunction with the VDF–HFP–CTFE terpolymer film. 0.625 Ah soft packaged graphite—$LiCoO_2$ test cells have been fabricated containing either plasticised VDF–HFP–CTFE terpolymer films or porous VDF–HFP–CTFE terpolymer films as separator. The measured porosities of the porous VDF–HFP–CTFE terpolymer films, which were 22 μm thick, were between 150 and 200 Gurley s. Sample cells were filled with liquid electrolyte containing $LiPF_6$ in a mixture of ethylene carbonate and ethyl methyl carbonate. All cell assembly and electrolyte filling operations were performed in a dry room (dew point −40 °C).

Cell testing was carried out using a Maccor Series 4200 test rig. Rate and cycle tests were carried out at 20 °C. Temperature testing was carried out in an environment controlled at the selected temperature and cells were stabilised for 6 h at the selected temperature prior to testing.

3. Results and discussion

Table 1 gives data for the uptake of 2EC/PC by the polymer samples at 21, 40 and 60 °C. Increased solvent uptake is observed with increasing temperature. As can be seen from this data, the VDF–HFP–CTFE terpolymer film has a greater capacity for solvent absorption compared to a homopolymer PVdF. Although a significant solvent uptake was measured at 60 °C, the film maintained its structural integrity.

Table 1
2EC/PC uptake by polymer films after 72 h as a function of temperature

Polymer films	Weight variation after absorption (%)		
	21 °C	40 °C	60 °C
Homopolymer PVdF SOLEF® 1015	22.3	23.3	33.0
Copolymer VDF–HFP SOLEF® 21216	36.7	45.1	Gel
Terpolymer VDF–HFP–CTFE	35.1	39.8	112.6

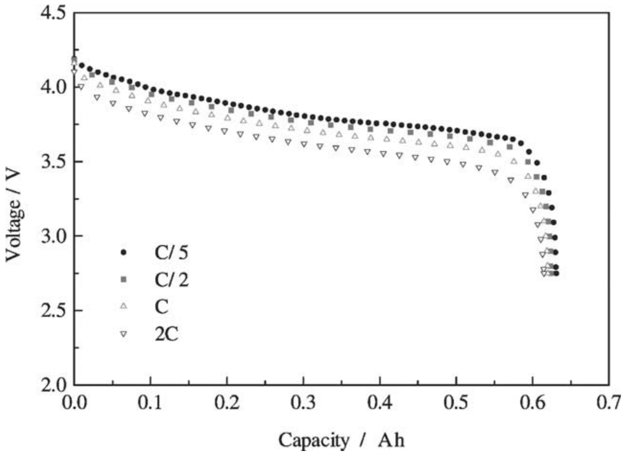

Fig. 1. Rate performance of a cell containing a porous VDF–HFP–CTFE terpolymer film.

Fig. 1 shows the rate performance of a graphite—$LiCoO_2$ cell containing a porous VDF–HFP–CTFE terpolymer film. Ninety-eight percent of Rated Capacity (0.625 Ah) was measured at 2*C* rate. This cell had a gravimetric energy density of 161 mAh g^{-1}.

The *C* rate cycle performance of a graphite—$LiCoO_2$ cell containing a porous VDF–HFP–CTFE terpolymer film is shown in Fig. 2. This cell was cycled at *C* rate between the voltage limits of 4.2–3.0 V, with every 20th cycle at *C*/5 rate

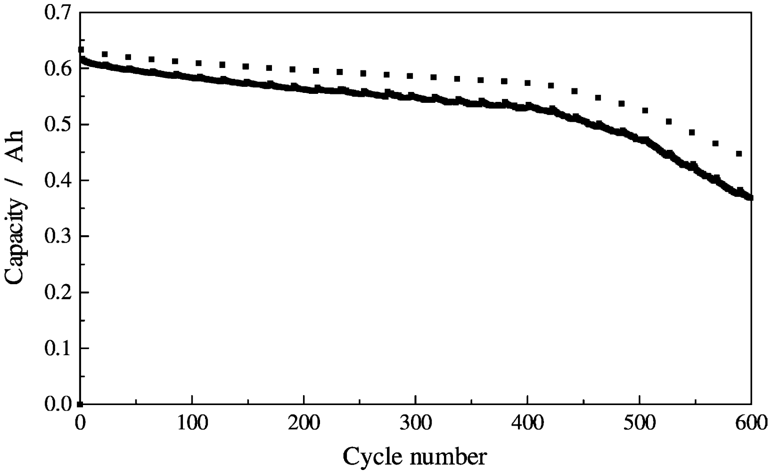

Fig. 2. Cycle performance of a cell containing a porous VDF–HFP–CTFE terpolymer film (see text for details).

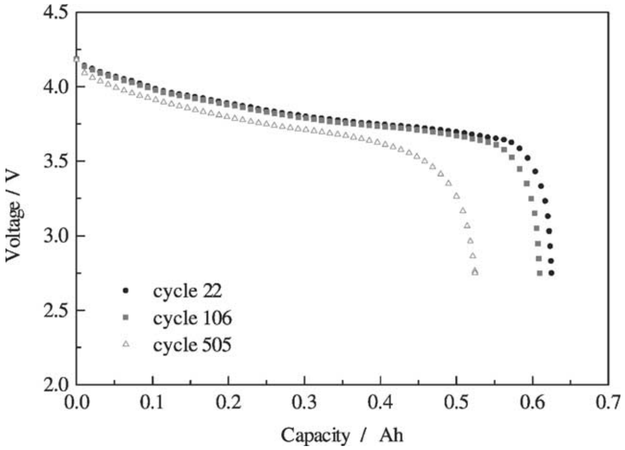

Fig. 3. *C*/5 rate discharge curves of a cell containing a porous VDF–HFP–CTFE terpolymer film as a function of cycle number.

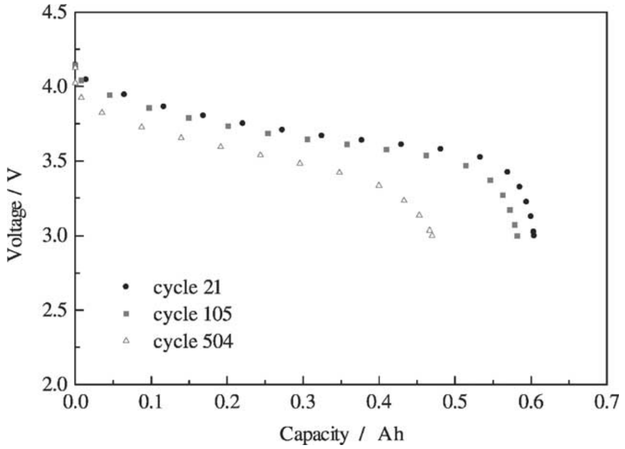

Fig. 4. *C* rate discharge curves of a cell containing a porous VDF–HFP–CTFE terpolymer film as a function of cycle number.

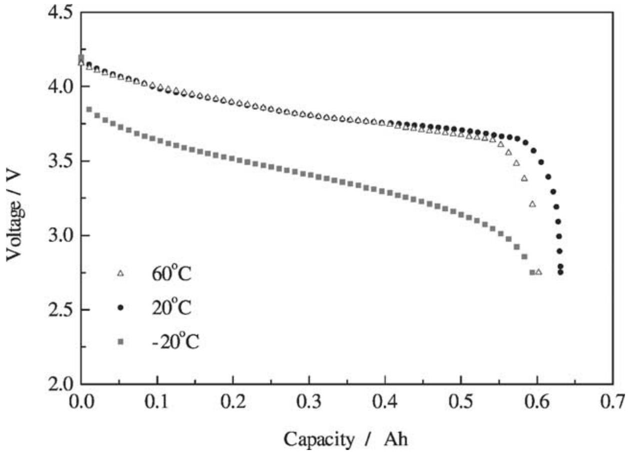

Fig. 6. *C*/5 rate discharge curves of a cell containing a porous VDF–HFP–CTFE terpolymer film as a function of temperature.

between the voltage limits of 4.2 and 2.75 V. Four hundred and fifty-four cycles were obtained at *C* rate to 80% of Rated Capacity. The data show a gradual increase in cell resistance with cycling. *C*/5 rate discharge curves for cycles 22, 106 and 505 are shown in Fig. 3, and *C* rate discharge curves for the preceding cycles are shown in Fig. 4. The effect of the increasing cell resistance is more evident for cycles at the higher rate. The cause of the capacity fade after 500 cycles has not yet been investigated. Electrolyte formulation and amount have not yet been optimised for cells of this type and this may be a factor in the rate of degradation.

The effect of temperature on both *C* and *C*/5 rate performance has been determined. Fig. 5 shows the discharge performance of a cell tested at *C* rate at a range of temperatures. Fifty-two percent of capacity obtained at 20 °C was achieved at −20 °C at *C* rate. Fig. 6 shows the discharge performance of a cell tested at *C*/5 rate at a range of temperatures. Ninety-four percent of capacity obtained at 20 °C was achieved at −20 °C at *C*/5 rate.

Fig. 7 shows the cycle performance of a cell tested at *C*/5 rate, cycled between voltage limits of 4.2–2.75 V containing two 5 μm thick plasticised VDF–HFP–CTFE terpolymer films as separator. Such polymer films were produced using dimethyl carbonate as casting solvent. Due to the nature of the coating process, some residual DMC may be left in the

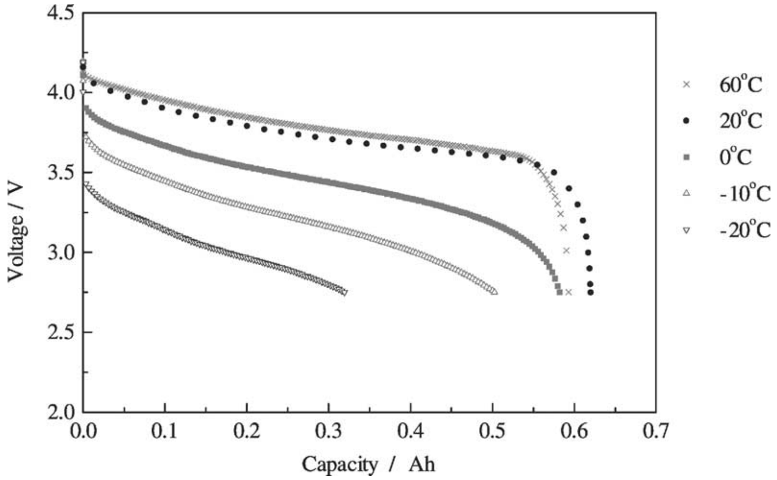

Fig. 5. *C* rate discharge curves of a cell containing a porous VDF–HFP–CTFE terpolymer film as a function of temperature.

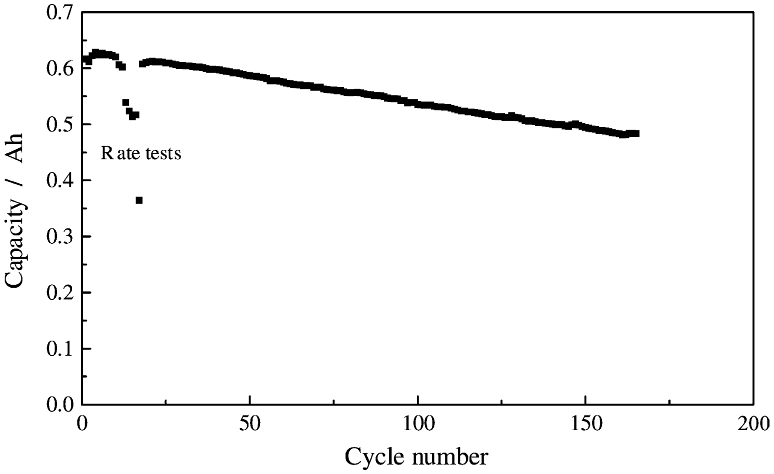

Fig. 7. *C*/5 cycle performance of a cell containing a plasticised VDF–HFP–CTFE terpolymer film.

film. These films can be produced as thin layers, 4–5 μm thick but with sufficient mechanical strength to enable cell fabrication. Rate performance for cells of this configuration was poorer than that measured for cells containing porous VDF–HFP–CTFE terpolymer films, for example, 59% of Rated Capacity was measured at 2*C* rate. Changes to plasticiser type and amount may give rise to improvements in high rate performance. Stable cycle behaviour was observed for this cell (Fig. 7).

4. Conclusions

A VDF–HFP–CTFE terpolymer has been used to produce porous and plasticised polymer films for use as cell separators. Thin, 4–5 μm plasticised polymer films have been produced with good mechanical properties. Improved cell performance was observed for cells containing porous polymer films. 0.625 Ah soft packaged graphite—$LiCoO_2$ test cells have been fabricated containing porous VDF–HFP–CTFE terpolymer films as separator. Ninety-eight percent of Rated Capacity was measured at 2*C* rate. Four hundred and fifty-four cycles were obtained at *C* rate to 80% of Rated Capacity.

Significant 2EC/PC solvent uptake was measured at 60 °C for VDF–HFP–CTFE terpolymer films but structural integrity was maintained.

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