



# Use of grafted PVdF-based polymers in lithium batteries

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## Abstract

Modifications to the properties of PVdF have been achieved by grafting. Selection of the appropriate monomer has led to an improvement in the adhesion of composite electrodes to current collectors, increased electrolyte solvent uptake and increased the range of solvents for homopolymer PVdF at room temperature. Graphite — LiCoO<sub>2</sub> cells containing such modified PVdF-based polymers have demonstrated good rate performance and stable cycle life. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Rechargeable lithium batteries; PVdF; Grafted polymers

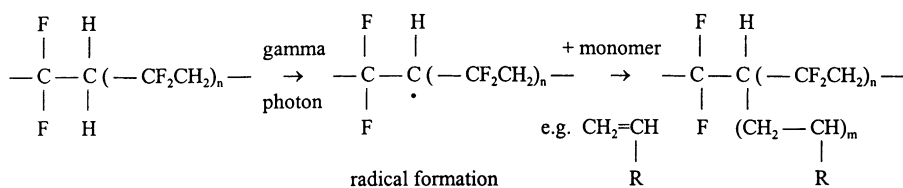
## 1. Introduction

Many Li-ion batteries and Li-ion polymer batteries contain PVdF-based polymers as electrode binders [1] and gel electrolytes [2]. Whilst PVdF-based polymers show good chemical and electrochemical stability in the Li-ion cell environment, their performance can be improved by use of grafted additives [3]. Areas that have been considered for

A range of monomers have been grafted onto PVdF-based polymers and assessed for these properties.

## 2. Experimental

Radiation grafting is carried out according to the following reaction:



where R is a functional group

development include

1. improvement of the adhesion of the electrodes to current collectors [4,5];
2. development of a thin conductive layer on current collectors;
3. modification of the solubility characteristics of the polymer;
4. modification of polymer properties to increase uptake of electrolyte.

The PVdF powder was irradiated by a cobalt-60 gamma source for a total dose of 10 kgray, at a dose rate of 1 kgray h<sup>-1</sup>. The irradiated PVdF powder was then placed in a reaction vessel containing a de-oxygenated aqueous solution of, for example, acrylic acid (10% by weight) which also contained ferrous sulphate (0.02 M) as a homopolymerisation inhibitor. This reaction mixture was held at 80°C and the progress of the reaction was monitored at intervals by taking a sample of the mixture and determining the remaining concentration of the acid by titration with sodium hydroxide.

After a few hours, when the desired consumption of acrylic acid had been achieved, the resulting graft copolymer powder was washed several times with deionised water, and

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then dried in a vacuum oven for 24 h at 50°C. The graft weight of the polymer was determined from the increase in weight of the polymer.

Composite electrodes for adhesion tests were produced by coating a slurry containing graphite, PVdF-g-acrylic acid (AA) and plasticisers onto a copper current collector. Peel tests were performed to ASTM D1876-72 using samples of dimensions 30 cm × 2.5 cm with a 22.5 cm bonded length. The samples were tested on a Lloyd M5K tensile tester with a 50 N load cell and fitted with soft grips for the foils. The crosshead speed was 254 mm min<sup>-1</sup>. Each sample consisted of two copper foils with a layer of the composite electrode composition sandwiched between them.

The use of dimethyl acrylamide (DMAM) has been evaluated as a grafting monomer on to PVdF to modify the solubility characteristics of PVdF. Homopolymer PVdF is soluble in aprotic polar solvents at room temperature, such as dimethyl acetamide, dimethyl formamide and *N*-methyl pyrrolidinone.<sup>1</sup> However, homopolymer PVdF grafted with 15 wt.% dimethyl acrylamide is soluble in acetone, e.g. a 9 wt.% solution of PVdF-g-DMAM (Solef 1015) in acetone could be produced. Such modifications to the polymer characteristics increase the options available for mix formulation.

The hydrophilic nature of the DMAM group can also increase the amount of electrolyte uptake by the polymer film. Cyclic and alkyl carbonates are typically used as electrolyte solvents in lithium batteries. A series EC/PC (1:1 by volume) absorption tests were carried out at 40 and 60°C on polymer samples of dimension 38 mm × 32 mm and of thickness 80–100 μm.

Test cells were fabricated by adopting a flat-wound cell design using porous electrodes in conjunction with a PVdF-based polymer film. Both plasticised PVdF-g-DMAM polymer films cast from an appropriate solvent and porous PVdF-g-DMAM polymer films fabricated using a solvent/non solvent method have been produced. Sample cells were filled with liquid electrolyte containing LiPF<sub>6</sub> in a mixture of alkyl and cyclic carbonates. All cell assembly and filling operations were performed in a dry room (dew point -40°C).

Batches of 0.6 Ah graphite — LiCoO<sub>2</sub> cells have been fabricated which contain such polymer films. Cells were put on test using an initial test regime of 0.2 C to 4.2 V plus 2 h potentiostatic hold at 4.2 V, followed by discharge at 0.2 C to 2.75 V. After initial cycles, rate tests were carried out on sample cells.

### 3. Results and discussion

An improvement in the adhesion of electrodes containing PVdF-based polymers to metal current collectors has been obtained by use of acrylic acid (AA) or methacrylic acid (MAA) grafted PVdF. The results of the peel tests carried out

Table 1

Effect of use of PVdF-g-AA on adhesion of composite anode to copper current collector

Mean value of three samples	Average load, <i>N</i>	Maximum load, <i>N</i>	Average strength, <i>N</i> (mm <sup>-1</sup> )
PVdF	0.107	0.525	0.0043
PVdF-g-AA	0.222	0.908	0.0089

on composite graphite anodes are given in Table 1. It can be seen that the adhesion of the composite electrode to the copper current collector is significantly improved by use of PVdF-g-AA as electrode binder. Delamination of electrodes is a contributing factor to capacity decline on cycling of Li-ion cells and it is anticipated that an improvement in adhesion will lead to improved cycle performance.

The amount of EC/PC (1:1 by volume) uptake by polymer samples at 40 and 60°C has been determined. Results for Solef 1015 PVdF are given in Tables 2 and 3, data for PVdF/HFP copolymer 20512 are given in Table 4. The EC/PC uptake increased with increasing temperature.

In general, PVdF-g-AA samples showed similar rates of EC/PC uptake to ungrafted polymer samples, but the amount of EC/PC uptake of PVdF-g-MAA samples was less. This may be due to the presence of the methyl group in place of hydrogen which may hinder absorption or to the less hydrophilic nature of MAA compared to AA. In addition, as the graft weight of monomer is increased, the effects of hydrogen bonding increases, thus, limiting EC/PC uptake due to restriction of the network. In all cases, the uptake of EC/PC by PVdF-g-DMAM samples was greater than ungrafted samples.

The rate performance of a graphite — LiCoO<sub>2</sub> cell containing a porous PVdF-g-DMAM polymer film has been evaluated. A total of 89% of rated capacity (0.63 Ah) was measured at the 2 C rate, Fig. 1.

The cycle performance of a graphite — LiCoO<sub>2</sub> cell containing a plasticised PVdF/HFP-g-DMAM polymer film

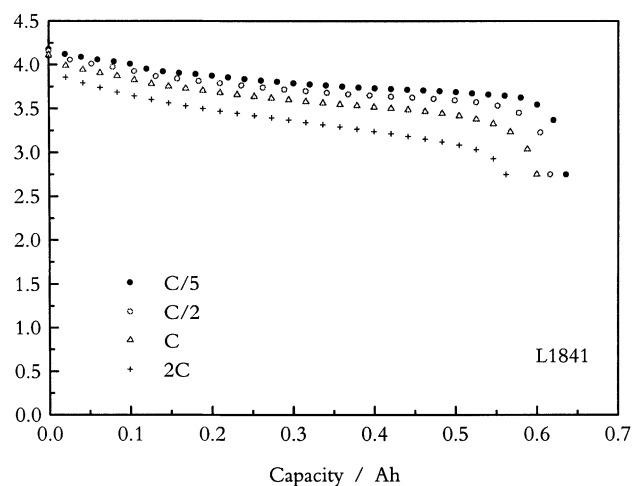


Fig. 1. Rate performance of cell containing porous PVdF-g-DMAM polymer film.

<sup>1</sup> Solef — polyvinylidene fluoride from Solvay, properties.

Table 2  
EC/PC absorption by polymer films based on Solef 1015 PVdF at 40°C<sup>a</sup>

Polymer	Ungrafted (%)	10%-g-AA (%)	15%-g-AA (%)	22%-g-MAA (%)	17%-g-DMAM (%)
24 h	25.7	23.9	26.1	17.1	34.2
72 h	26.8	24.7	27.1	19.5	34.7

<sup>a</sup> Weight variation after immersion %.

Table 3  
EC/PC absorption by polymer films based on Solef 1015 PVdF at 60°C<sup>a</sup>

Polymer	Ungrafted (%)	15%-g-AA (%)	22%-g-MAA (%)	17%-g-DMAM (%)
24 h	26.4	31.6	22.8	38.0

<sup>a</sup> Weight variation after immersion %.

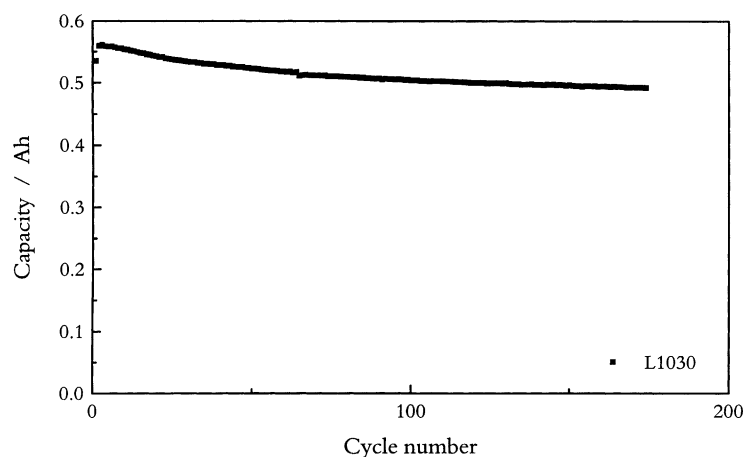


Fig. 2. Cycle performance of graphite — LiCoO<sub>2</sub> cell containing plasticised PVdF/HFP-g-DMAM polymer film.

Table 4  
EC/PC absorption by polymer films based on Solef 20512 PVdF/HFP at 40°C<sup>a</sup>

Polymer	Ungrafted (%)	15%-g-AA (%)	22%-g-DMAM (%)
24 h	23.7	25.7	28.8
72 h	24.5	26.5	29.8

<sup>a</sup> Weight variation after immersion %.

has been evaluated. Cells containing such electrolyte films exhibit stable cycle behaviour as illustrated in Fig. 2.

#### 4. Conclusions

Modifications to the properties of PVdF-based polymer have been achieved by grafting. Selection of the graft

monomer provides a range of options, such as increased adhesion to metal foils, increased electrolyte solvent uptake and changes in solubility characteristics. Graphite — LiCoO<sub>2</sub> cells containing such modified PVdF-based polymers have demonstrated good rate performance and stable cycle life.

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