

Short communication

Separator-free rechargeable lithium ion cells produced by the extrusion lamination of polymer gel electrolytes

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Received 15 March 2005

Available online 18 August 2005

Abstract

Polymer gel electrolytes (PGE) based on polyvinylidene fluoride (PVDF), lithium salts and appropriate solvent systems, developed at Leeds University, have been shown to form tough rigid films with conductivities approaching $10^{-2} \text{ S cm}^{-1}$. A continuous process has now been developed for the construction of rechargeable lithium cells by extruding the PGE as a melt and directly laminating between the anode and cathode electrodes. On cooling, the solid PGE acts as electrolyte and separator and binds the cell laminate together from within requiring no external case. This process has been successfully applied for the fabrication of cells with electrodes developed by SpectraPower Inc. in a commercial process enabling cell laminates with PGE thickness less than 0.1 mm and with energy densities approaching 170 Wh kg^{-1} . A prototype manufacturing facility has been set up to produce rechargeable cells of high specific capacity and high energy density. Future developments will enable rechargeable lithium ion cells to be produced on a continuous process as flat sheets opening the way for novel battery geometries.

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Keywords: Rechargeable lithium batteries; Polymer gels

1. Introduction

The pioneering research of Wright [1] and Armand et al. [2] has led to the development of ionically conducting polymers for use in rechargeable lithium batteries. Research at Leeds University in this area commenced in 1980 as part of the Anglo-Danish battery project and has continued with the support of EPSRC, initially as part of their initiative in *Electroactive Polymers* and then as a major research programme within the IRC in Polymer Science and Technology, where Professor I.M. Ward was the first Director.

At first, systems based on polyethylene oxide were studied [3–5] but later research was undertaken on highly plasticised polyacrylamides [6], liquid crystalline systems [7,8], crown ether and comb polymers [9–11]. By 1990, it had

become apparent that a novel approach was required if materials with sufficiently high conductivities ($>10^{-2} \text{ S cm}^{-1}$) and adequate mechanical properties (stiffnesses $> 10^3 \text{ kPa}$) could be produced. This led to the invention in 1991 of thermally reversible polymer gel electrolytes [12–16] based primarily on polyvinylidene fluoride (PVDF) and their application to electrochromic devices and rechargeable lithium batteries.

In 1996, Gelectrix Ltd. was set up under the auspices of Leeds Innovations (University of Leeds) with Prof. I.M. Ward as Managing Director and Dr. H.V.St.A. Hubbard as Chief Scientist, to develop and exploit the patented polymer gel technology for use in lithium ion rechargeable cells. Smart I and Smart II awards were obtained in open competition from the UK Department of Trade and Industry to examine the feasibility of using polymer gel electrolytes as electrolyte separators in cells. This was successfully demonstrated and a processing route for the continuous production of cells established.

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Table 1
The various polymer gel electrolyte materials investigated

Polymer	Solvent	Salt
Principal		
PVDF	PC	LiBF ₄
	EC	LiPF ₆
Others		
PET	DEE	LiCF ₃ SO ₃
PHBA	DMF	LiClO ₄
POM	Tetraglyme	
MXD6	DMA	
Nylon 6.6	NMP	
PMMA	DMSO	

PVDF: poly(vinylidene fluoride); PET: poly(ethylene terephthalate); PHBA: poly(hydroxybutyric acid); MXD6: poly(*m*-xylene adipamide); POM: poly(oxymethylene); PMMA: poly(methylmethacrylate); TGm: tetraglyme [CH₃(OCH₂CH₂)₄OCH₃]; DMF: *N,N*-dimethylformamide; DMA: *N,N*-dimethylacetamide; NMP: *N*-methyl pyrrolidone; EC: ethylene carbonate; PC: propylene carbonate; DMSO: dimethylsulfoxide; DEE: diethoxyethane.

2. Polymer gel electrolytes

For polymers, which form crystalline phases on cooling from the melt, thermoreversible gels can be made, which provide enhanced processability and a firm robust gel phase below the melt temperature. A typical gel is prepared from a mixture of polymer, solvent and salt, which is then heated and stirred until a homogeneous melt is formed; upon cooling, a thermoreversible gel is formed.

Table 1 lists examples of the polymer gel electrolyte systems investigated at Leeds. As a result of this initial study it was found that the PVDF gels showed superior performance in terms of mechanical and conductive properties compared with gels made with other polymers and subsequent research has focussed on the PVDF gels.

Fig. 1 shows the ionic conductivity behaviour over a range of temperatures and compares the gel electrolytes with the corresponding liquid electrolyte for some polymer electrolytes. Room temperature conductivities are above

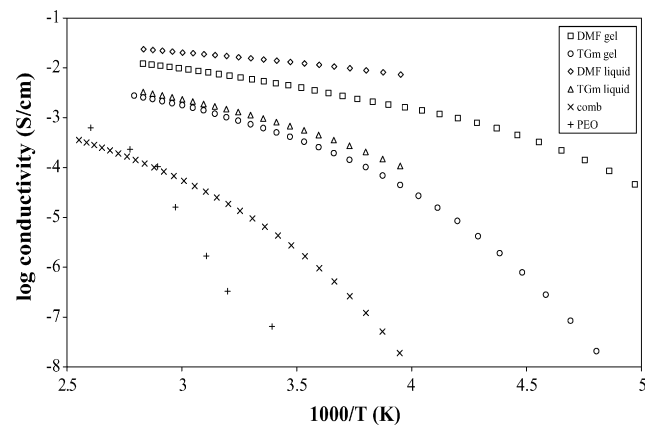


Fig. 1. Ionic conductivities of some gels, corresponding liquid electrolytes and polymer electrolytes compared.

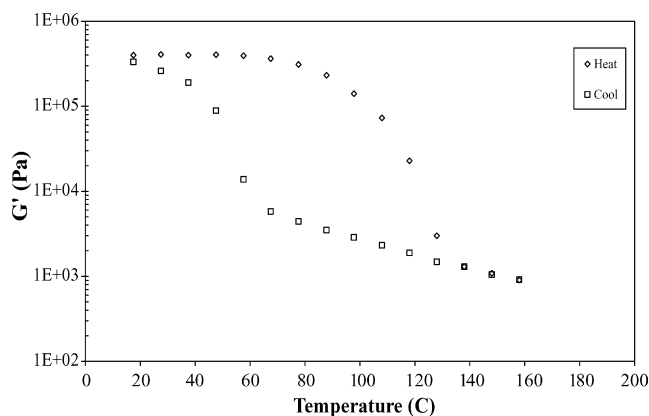


Fig. 2. Complex modulus G^* for 30% PVDF–tetraglyme–LiCF₃SO₃ sample (heating rate 2 °C min⁻¹) showing the difference between melting and gelation temperatures.

10⁻³ S cm⁻¹ for all the gel systems and for gels made with polar solvents, such as DMF conductivities are greater than 10⁻³ S cm⁻¹ at -20 °C.

Extensive studies have been undertaken using pulse field gradient spin echo (PFG) NMR measurements [17–20], in conjunction with measurements of ionic conductivity and solution viscosity [21,22] on electrolyte solutions, together with measurements on the gel electrolytes [15,16]. These studies have shown how the ionic conductivity can be readily understood in terms of the ionic mobilities and that these relate in turn to the solution viscosities (via Stokes–Einstein equation) and the ionic conductivity (via Nernst–Einstein equation). Comparison of the gel electrolyte behaviour and the electrolyte solution behaviour, including NMR T_1 measurements as well as PFG measurements, showed that the ionic mobilities in the former are very little affected by the polymeric environment so that the PVDF essentially acts to contain the liquid electrolyte in a non-interacting rigid environment.

Fig. 2 shows the complex modulus G^* of the thermoreversible gels as a function of temperature. The figure clearly shows that the temperature at which the gel melts is very much higher than that at which the gel is formed on cooling. The gelation behaviour of these thermoreversible gels is a function both of temperature and time. This unique property of these gels is exploited in the fabrication of cells by extrusion lamination of the polymer gel electrolyte (PGE).

3. Initial feasibility programme

The SMART I feasibility programme consisted of making and testing small test cells using various combinations of electrodes and compositions of thermoreversible gel electrolytes (Table 2). The electrodes and gel layer were held in place by pressure and in all cases the gel electrolyte was based on PVDF.

Table 2
Lithium and lithium-ion rechargeable cells

Anode (–)	Gel electrolyte		Cathode (+)
	PVDF–solvent	Salt	
Graphite	PC:EC	LiBF ₄	LiNiO ₂
Petroleum coke	EC:DEE	LiPF ₆	LiCoO ₂
Lithium metal	PC:DME	LiCF ₃ SO ₃	LiNi _{0.8} Co _{0.2} O ₂
	EC:EMC	LiClO ₄	LiMn ₂ O ₄ (4 V)
	EC:DMC		LiMn ₂ O ₄ (3 V)
	TGm		
Carbon black			Carbon black
Binders			Binders
Current collector: copper			Current collector: aluminium; nickel

DME: dimethoxyethane (monoglyme); EMC: ethyl methyl carbonate; DMC: dimethyl carbonate.

4. Extrusion lamination process

Following the successful completion of trials on test cells, which demonstrated that the PGE did not impair the performance of cells compared with liquid cells using a permeable separator, a continuous extrusion lamination process has been developed [23].

In this single continuous fabrication process, a strong robust laminate is produced in which the PGE (i) holds the laminate together (requiring no external pressure), (ii) separates the electrodes and (iii) provides high lithium ion conduction.

Fig. 3 outlines the extrusion lamination process. The electrodes in the form of strips of precoated foil are prewound onto storage rolls (A and B) and fed via guide rollers (C and D) over heated rollers through the “nip” (E).

The polymer gel electrolyte is extruded through a die (G) in the form of a thin viscous tape. The extrudate is layered onto the electrode foils as they pass over the heated lamination

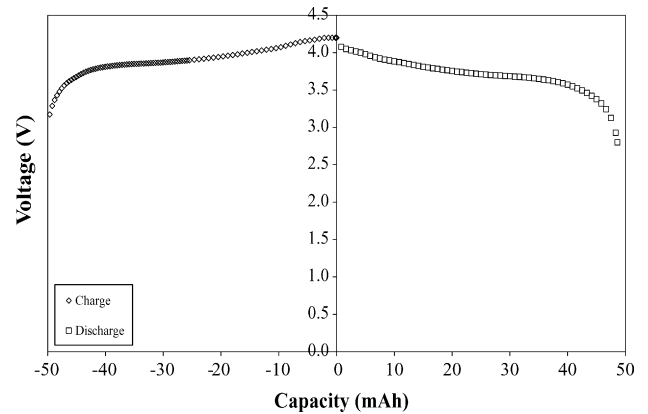


Fig. 4. Charge and discharge curves of laminated cell using PVDF–EC:PC–LiBF₄ gel electrolyte with SpectraPower electrodes.

rollers heated at a lower temperature than that of the melt and into the nip where the whole assembly is laminated together. The laminate then cools the PGE gels making a robust bonded laminate (H).

In the pilot apparatus used for the development work, the electrodes are in the form of precoated foils 40 mm wide. The entire process is housed in a dry chamber. A proportion of the gel solvent can be incorporated as volatile solvent (e.g. DEE, DEC, EMC, DMC).

The precoated electrode foils are typically a carbonaceous material as anode on copper foil and a high voltage lithium intercalation oxide as cathode (typically, LiMnO₂ or LiCoO₂, etc.) on aluminium foil. Typical cathode loadings are 10–25 mg cm⁻² and anode loadings of 4–10 mg cm⁻². The electrode material needs to adhere well to the foils and needs to resist the gel solvent to be used at the temperature of the lamination.

Fig. 4 shows typical cell cycling behaviour for a cell using commercial SpectraPower electrodes with cathodes com-

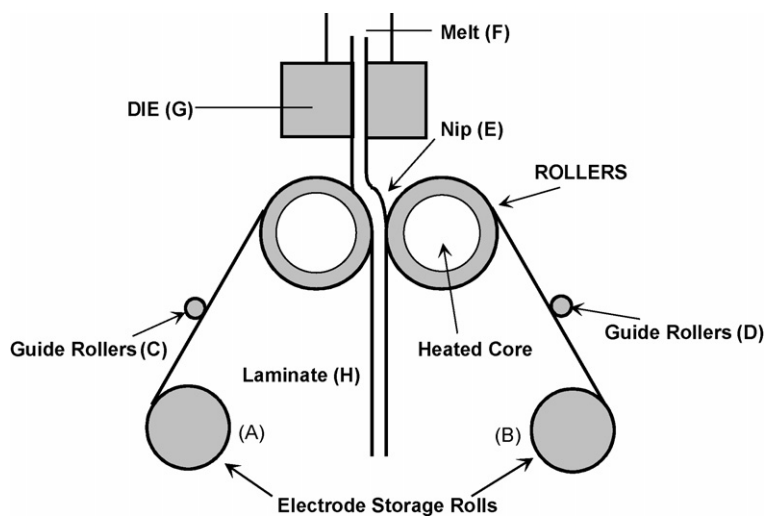


Fig. 3. Extrusion lamination processing arrangement. (A and B) electrode storage rolls; (C and D) guide rollers; (E) lamination nip; (F) extruder barrel (G) die; (H) laminate.

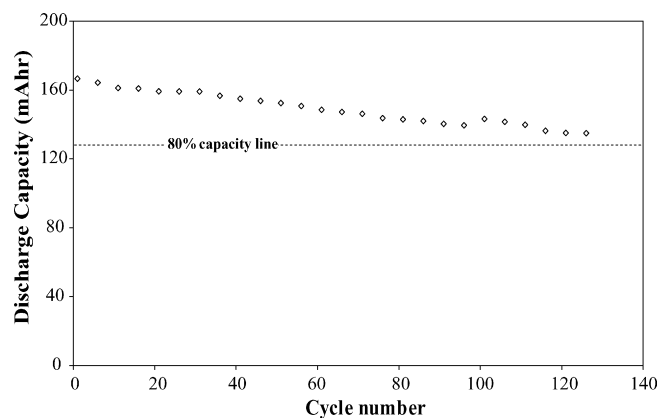


Fig. 5. Typical cycle life performance.

Table 3
Cell specification available with the technology

	Achieved	Projected
Nominal voltage	3.8	3.9
Gel thickness (μm)	50	25
Overall cell thickness (μm)	280	220
Capacity (mAh cm^{-2})	2.4	2.5
Energy (mWh cm^{-2})	8.9	9.7
Mass (mg cm^{-2})	60	52
Specific energy (Wh kg^{-1})	150	185
Volumetric energy density (Wh l^{-1})	320	440

prising lithium nickel cobaltous oxide and a carbonaceous anode.

Fig. 5 shows a typical cycle life performance and Table 3 the cell specification available at this early stage of development.

5. Advantages of this system and the future potential of this technology

Polymer gel electrolytes prepared using PVDF have the particular advantage of being mechanically robust, providing high conductivity and are processable as a thermoreversible gel. The single continuous fabrication process described produces a strong tough laminate in which the PGE (i) holds the laminate together internally (requiring no external pressure), (ii) separates the electrodes and (iii) provides high lithium ion conduction.

The essential simplicity of this single process enables a high speed continuous process to produce the packaged battery; the dryness requirement, necessary for any lithium based system, is essentially confined to the small space at the point of fabrication, i.e. between the extruder die and the lamination nip. The cell can be packaged immediately after lamination. Furthermore, the gel processing technology can be adapted to most lithium ion based electrode systems.

Future possibilities for this technology include photo-voltaics, electrochromics and sensors, in addition to present applications targeted for batteries and smart cards.

Acknowledgements

The initial funding for the gel electrolyte technology came from the UK Engineering and Physical Sciences Research Council, through the Interdisciplinary Centre in Polymer Science and Technology during the period 1989–1995. Gelectrix Ltd. was set up in 1996 with funding from the UK Department of Trade and Industry and Leeds Innovations and has involved collaboration with Cambridge Consultants Ltd. and further financial support from Isotek Ltd. More recently, the gel electrolyte technology has been supported by the University of Leeds and British Technology Group (BTG) and has involved collaboration between the Leeds team and SpectraPower Inc. who have provided the electrodes.

References

- [1] P.V. Wright, Br. Polym. J. 7 (1975) 319.
- [2] M.B. Armand, J.M. Cabagno, M.J. Duclot, in: P. Vashishta, J.W. Mundy, F.K. Shenog (Eds.), Fast Ion Transport in Solids, Elsevier, Amsterdam, 1979, p. p. 137 (Section III).
- [3] D.J. Bannister, G.R. Davies, I.M. Ward, J.E. McIntyre, Polymer 25 (1984) 1291.
- [4] D.J. Bannister, G.R. Davies, I.M. Ward, J.E. McIntyre, Polymer 25 (1984) 1600.
- [5] P.G. Hall, G.R. Davies, J.E. McIntyre, I.M. Ward, D.J. Bannister, K.M.F. LeBroeq, Polym. Commun. 27 (1986) 98.
- [6] S.A. Dobrowski, G.R. Davies, J.E. McIntyre, I.M. Ward, Polymer 32 (1991) 2887.
- [7] I.M. Ward, J.E. McIntyre, G.R. Davies, S.A. Dobrowski, S.R. Mirrezaei, H.V.St.A. Hubbard, Electrochem. Acta 37 (1992) 1479.
- [8] H.V.St.A. Hubbard, S.A. Sills, G.R. Davies, J.E. McIntyre, I.M. Ward, Electrochem. Acta 43 (1998) 1239.
- [9] L. Collie, D. Parker, C. Tachon, H.V.St.A. Hubbard, G.R. Davies, I.M. Ward, S.C. Wellings, Polymer 34 (1993) 1541.
- [10] J.E. Denness, D. Parker, H.V.St.A. Hubbard, J. Chem. Soc. Perkin Trans. 2 (1994) 1445.
- [11] H.V.St.A. Hubbard, J.P. Southall, J.M. Cruickshank, G.R. Davies, I.M. Ward, Electrochem. Acta 43 (1998) 1485.
- [12] H.V.St.A. Hubbard, J.E. McIntyre, V. Rogers, I.M. Ward, International Patent Number PCT/GB92/01781, Ionically Conductive Polymer Gels (filed 29 September 1992; priority date 3.10.1991).
- [13] A.M. Voice, J.P. Southall, V. Rogers, K.H. Matthews, G.R. Davies, J.E. McIntyre, I.M. Ward, Polymer 35 (1994) 3363.
- [14] A.M. Voice, G.R. Davies, I.M. Ward, Polym. Gels Networks 5 (1997) 123.
- [15] I.M. Ward, M.J. Williamson, H.V.St.A. Hubbard, J.P. Southall, G.R. Davies, J. Power Sources 81–82 (1999) 700.
- [16] M.J. Williamson, H.V.St.A. Hubbard, I.M. Ward, Polymer 40 (1999) 7177.
- [17] N. Boden, S.A. Leng, I.M. Ward, Solid State Ionics 45 (1991) 261.
- [18] I.M. Ward, N. Boden, J. Cruickshank, S.A. Leng, Electrochim. Acta 40 (1995) 2071.

- [19] M.J. Williamson, J.P. Southall, H.V.St.A. Hubbard, S.F. Johnston, G.R. Davies, I.M. Ward, *Electrochem. Acta* 43 (1998) 1415.
- [20] M.J. Williamson, J.P. Southall, I.M. Ward, *J. Chem. Phys.* 109 (1998) 7893.
- [21] J. Cruickshank, H.V.St.A. Hubbard, N. Boden, I.M. Ward, *Polymer* 36 (1995) 3779.
- [22] J.P. Southall, H.V.St.A. Hubbard, S.F. Johnston, V. Rogers, G.R. Davies, J.E. McIntyre, I.M. Ward, *Solid State Ionics* 85 (1996) 51.
- [23] I.M. Ward, H.V. St. A. Hubbard, P.L. Carr, F. Tyldesley, International Patent Number PCT/GB01/03937, Extruded Battery Components (filed 31 August 2001; priority date 1.9.2000).