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Journal of Power Sources 92 (2001) 272–276

JOURNAL OF
**POWER
SOURCES**

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Short communication

Polymeric gel electrolytes reinforced with glass-fibre cloth for lithium secondary batteries

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Received 29 February 2000; accepted 2 May 2000

Abstract

Polymeric gel electrolytes (PGE), based on polyacrylonitrile blended with poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP), which are reinforced with glass-fibre cloth (GFC) to increase the mechanical strength, are prepared for the practical use in lithium secondary batteries. The resulting electrolytes exhibit electrochemical stability at 4.5 V against lithium metal and a conductivity value of $(2.0\text{--}2.1)\times 10^{-3}\text{ S cm}^{-1}$ at room temperature. The GFC-PGE electrolytes show excellent strength and flexibility when used in batteries even if they contain a plasticiser. A test cell with LiCoO_2 as a positive electrode and mesophase pitch-based carbon fibre (MCF) as a negative electrode display a capacity of 110 mAh g^{-1} based on the positive electrode weight at the 0.2 C rate at room temperature. Over 80% of the initial capacity is retained after 400 cycles. This indicates that GFC is suitable as a reinforcing material to increase the mechanical strength of gel-based electrolytes for lithium secondary batteries. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium-ion battery; Polymer electrolyte; Glass-fibre cloth; Mechanical strength; Polymer gel electrolyte

1. Introduction

Secondary lithium-ion batteries are used as power sources for portable electronics, electric vehicles and electric-storage facilities. Polymeric gel electrolyte (PGE), which consists of a polymer matrix, a plasticiser and a lithium salt, have been extensively studied for application in lithium-based batteries because of their high ionic conductivity (over 10^{-3} S cm^{-1}) at room temperature [1–25]. Feuillade and Perche [1] were the first to prepare organic solid electrolytes by plasticising a polymer with the solution of an alkali metal salt in an aprotic solvent. Watanabe et al. [2] reported the ionic conductivity of a polyacrylonitrile (PAN) complex which consisted of ethylene carbonate (EC) or propylene carbonate (PC) as a plasticiser, and LiClO_4 as a salt. Tsuchida et al. [4] demonstrated that the conductivity does not depend on the concentration of the salt, but rather on the ratio of plasticiser to salt.

Though many PGE systems, e.g. PVdF, PMMA, PEO, PVC, have been studied, to date there has been no commercialisation of a lithium-based secondary battery using PGE as an electrolyte [16]. One of the crucial reasons appears to be the poor mechanical strength of PGEs, which does not allow an easy construction of a unit battery cell configuration. Therefore, it is necessary to increase the mechanical strength of GPE so that lithium-based batteries can be packaged in plastic and fabricated by an inexpensive manufacturing process which employs the lamination and packing processes commonly used in the plastic industry. In addition, PGE should have the ability to be geometrically compliant, a feature which allows it to be fabricated in the shape required by a wide variety of products [20].

The purpose of the present study is to seek an improvement in the mechanical strength of PGE, through the use of glass-fibre cloth (GFC) as a reinforcing material, so that the material can be applicable to lithium-ion batteries. In particular, PAN-based composite polymer electrolytes with GFC as a reinforcing agent have been prepared since these have better performance and safety than conventional polyether-based gel electrolytes for battery applications. Polymeric

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gels have been made by using polyacrylonitrile (PAN) blended with poly(vinylidene fluoride-co-hexafluoropropylene) (P(VdF-co-HFP)) to improve the creep-resistance properties of viscoelastic PAN gel.

2. Experimental

For the fabrication of polymeric gel, LiClO₄ (FMC Corp.) was dissolved in EC, PC and diethyl carbonate (DEC) (Merck chemicals). After complete dissolution, weighted amounts of PAN (Aldrich) and P(VdF-co-HFP) (Kynar 2801) were dissolved in the solution at 110°C. PGE–GFC films with a thickness of 40–80 μm were obtained by casting the gel solution onto a glass sheet substrate covered with a GFC with thickness of 38 μm in a dry argon box. The geometry and shape of the GFC designed and used in this experiment are shown in Fig. 1. The electrolyte composition of the PGE–GFC film is given in Table 1.

Electrochemical tests for PGE–GFC films were performed in an argon-filled glove-box by means of cyclic voltammetry and a frequency response analyser. Stainless-steel (Sus) and lithium metal were used as the working and the counter electrode, respectively. For these measurements, the samples of PGE–GFC film were cut into discs of 1.0 cm diameter and stacked between the Sus and Li metal electrodes, and then encapsulated in a PTFE cylindrical container with a diameter of 1.0 cm.

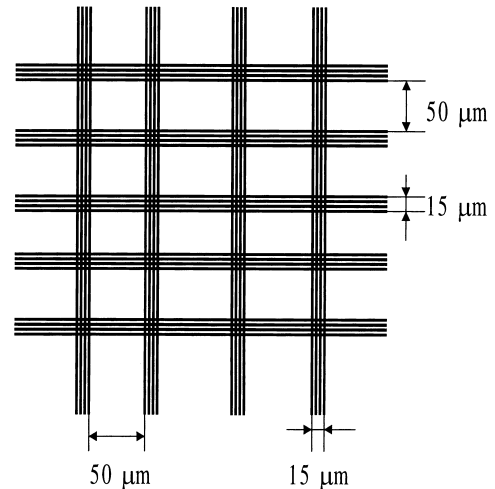


Fig. 1. Glass-fibre cloth design.

Cathode mixtures, consisting of 85 wt.% active material (LiCoO₂, Seimi Corp.), 10 wt.% Super-P, and 5 wt.% PVdF binder, were dissolved in 1-methyl-2-pyrrolidinone to obtain a slurry. The slurry was spread onto an aluminium foil and dried at 80°C for 20 h, followed by pressing with roll press. MCF (Petoca Corp.) on copper foil was used as the negative active-material. The preparation procedure was the same as that for the positive electrode. The electrodes have a surface area of 33 cm² and the configuration of test cell is shown in Fig. 2. Charge–discharge (Power Tech) experi-

Table 1
Composition (wt.%) of PGE–GFC film

Sample	GFC	Polymer		Plasticiser			LiClO ₄ salt
		PAN	P(VdF-co-HFP)	EC	PC	DEC	
GPE		8	0.8	37.2	37	13	4
PGE–GFC	4	8	1.6	36.7	36.7	13	4

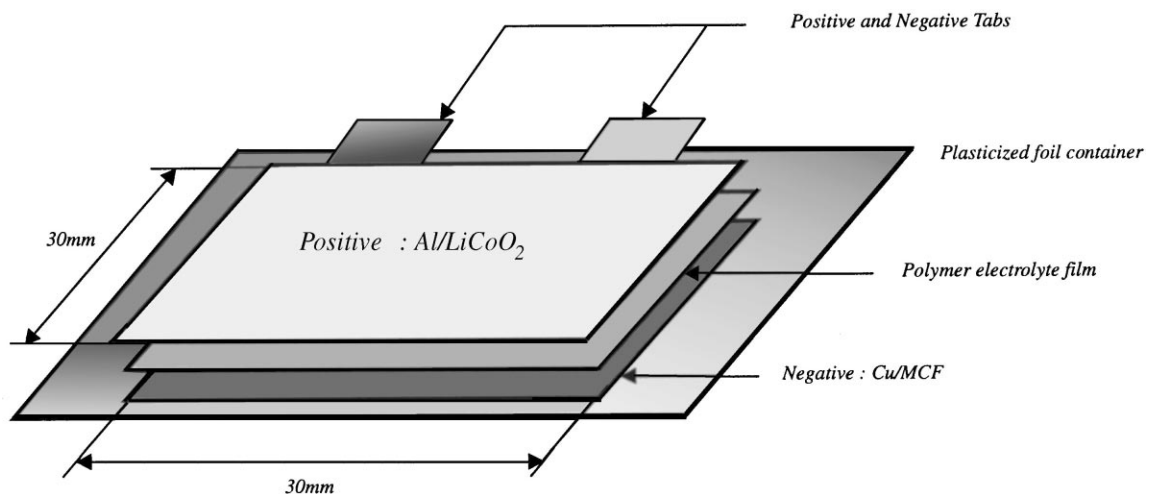


Fig. 2. Diagram of test cell.

ments were performed in the current density range of 1–5 mA cm⁻².

3. Results and discussion

The mechanical and physical properties of the prepared electrolytes have been investigated and typical burst strengths of the GFC and GFC–PGE composite electrolytes have been compared with that of commercial microporous polypropylene (Table 2). Table 3 summarises the measured bulk conductivity values of the GFC and GFC–PGE composite electrolytes. The conductivity of GFC–PGE electrolytes is almost the same with that of GPE without reinforcing materials [20–25]. This implies that the presence of the GFC in the gel does not diminish the ionic conductivity of electrolyte, rather it provides increased mechanical strength, ease of dimensional control, and ease of handling. These electrolytes represent an improvement in ionic conductivity over electrolyte structures which consist of microporous Celgard impregnated with various poly(tetraethylene glycol diacrylate) gels with conductivities of $(1.2–3.0) \times 10^{-4}$ S cm⁻¹. In addition, it has been reported [27–29] that when solid polymer electrolyte film based cross-linked polyethylene oxide is bent to 180°, cracks develop on the solid polymer electrolyte, as dictated by the cross-linking density. By contrast, the GFC–PGE is very flexible and does not crack even when bent.

Current–voltage response, used to check the electrochemical stability of PGE–GFC, are presented in Fig. 3. It can be seen that the anodic decomposition voltage limits are close to 5.0 V. This suggests that there is no decomposition of GFCs as well as any other components in the polymeric gel in this potential region.

In order to investigate the applicability of a PGE–GFC in lithium secondary batteries, charge and discharge experiments were carried out using a lithium-ion cell, namely, MCF/PGE–GFC/LiCoO₂. The voltage profiles obtained at

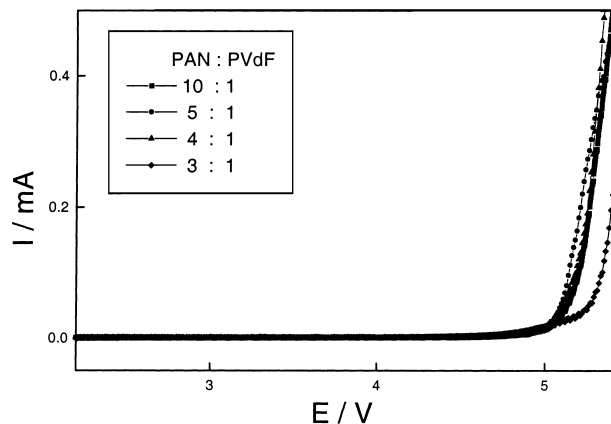


Fig. 3. Current–voltage response of PGE–GFCs.

the 0.2 C rate (1 mA cm⁻²) between 2.8 and 4.1 V for the initial five cycles are given in Fig. 4. The charge–discharge curves are very flat, which is a typical characteristic of a lithium-ion battery using graphite and LiCoO₂ as the negative and positive electrodes, respectively [17,26]. The cell has a capacity of 110 mA g⁻¹ based on positive-electrode weight. The rate capability shows that over 80% of the capacity at 5 mA cm⁻² can be obtained compared with that at 1 mA cm⁻² (Fig. 5). The temperature dependence of the discharge capacity is given in Fig. 6. The discharge capacity at –10°C is 71% of that at 25°C.

The cycling performance of the test cell is given in Fig. 7. The cell provides over 400 cycles with a drop in capacity of only ~20%. It is well-known that one of the main determinants of cycle-life is the creep phenomena observed in polymer gel electrolytes due to their viscoelasticity. The results presented here, however, suggest that the GFC shape of the reinforcing material is a very effective means of preventing the creep of polymer gel electrolyte between the electrodes and, thereby, maintaining dimensional stability.

Table 2

Comparison of mechanical strength of polymer electrolytes and microporous Celgard membrane

Sample	Thickness (μm)	Burst strength (kPa)
GFC–PGE	90	>1000
Celgard polypropylene	25	105
PGE	110	<2

Table 3

Ionic conductivity of polymer electrolytes at room temperature

Sample	Conductivity (S cm ⁻¹)
GFC–PGE	2.0×10^{-3}
PGE	2.1×10^{-3}

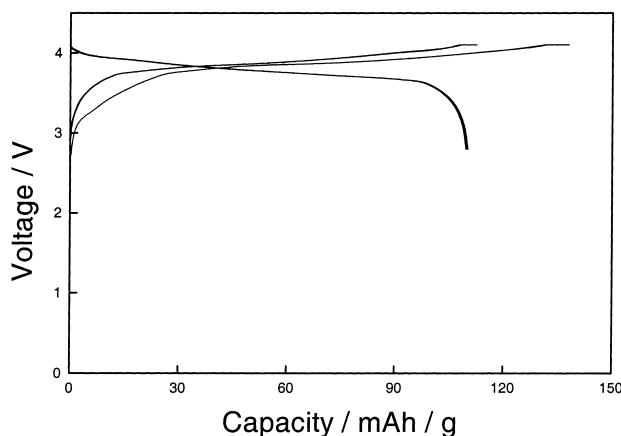


Fig. 4. Charge–discharge profiles of test cells.

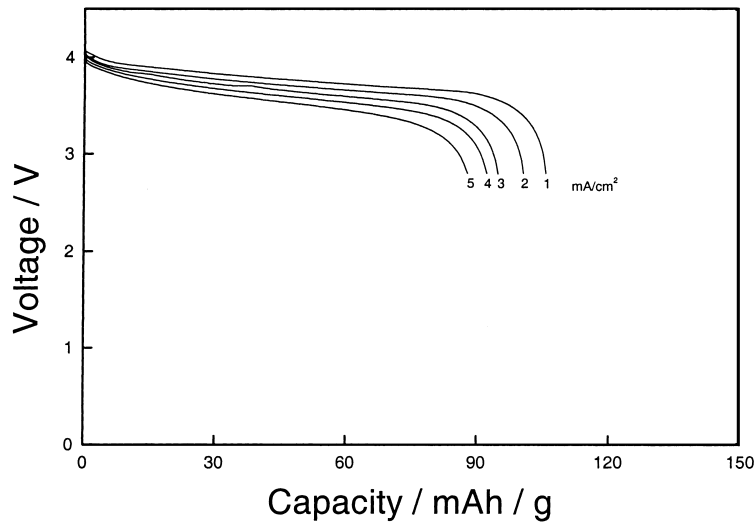


Fig. 5. Rate capability of cells according to discharge current density. Cell conditions are the same as in Fig. 4.

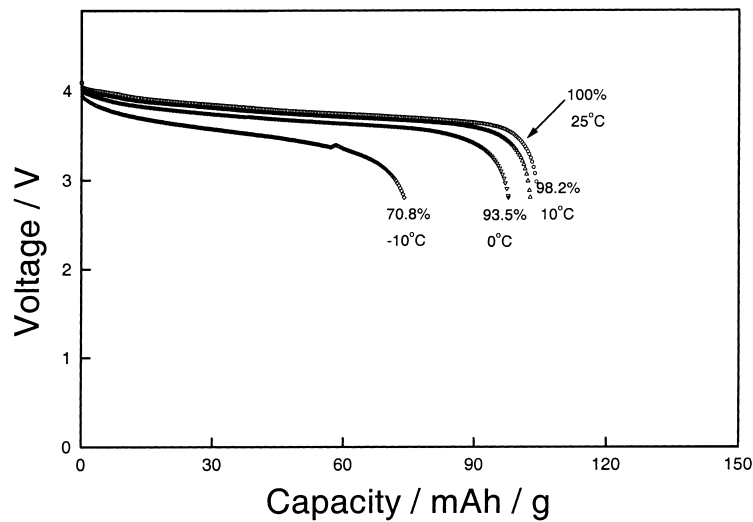


Fig. 6. Temperature dependence of discharge capacity of test cell at 0.2 C rate. Cell conditions are the same as in Fig. 4.

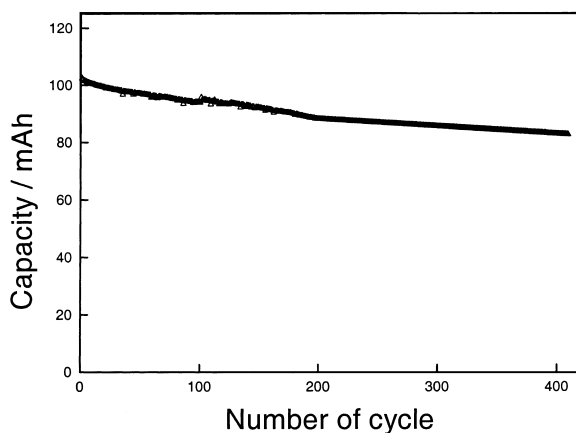


Fig. 7. Cycling performance of test cell. Cell conditions are the same as in Fig. 4.

4. Conclusions

Blended polymer gel electrolytes based on PAN and P(VdF-co-HFP), which are reinforced by GFC to increase the mechanical strength, have been prepared and tested for practical use in lithium-ion batteries. The resulting electrolytes exhibit electrochemical stability up to 5 V against lithium metal and a conductivity of $2.0 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature. The GFC-PGE has excellent mechanical strength and flexibility when used in batteries, even if it contains a plasticiser. A test cell using LiCoO_2 as the positive electrode and MCF as the negative electrode gives a capacity of 110 mAh g^{-1} based on the positive electrode weight at the 0.2 C rate at room temperature. The cell retains over 86% of initial capacity after 400 cycles. It is concluded from these results that GFC is suitable as a reinforcing

material to increase the mechanical strength of gel-based electrolytes for lithium-based secondary batteries.

Acknowledgements

Financial support for this work was provided by the Korea Energy Management Corporation R&D Management Center for Energy and Resources.

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