Poly(vinylidene fluoride-hexafluoropropylene)

(2001 9 3 , 2001 12 19)

Thermal and Electrical Properties of Poly(vinylidene fluoridehexafluoropropylene)-Based Proton Conducting Gel-Electrolytes

B. K. Choi[†] and S. H. Park

Department of Applied Physics, Dankook University, Seoul 140-714, Korea †e-mail: bkchoi@dankook.ac.kr
(Received September 3, 2001;accepted December 19, 2001)

ABSTRACT: Polymer electrolyte films consisting of poly(vinylidenefluoride-hexafluoro-propylene) (PVdF-HFP), H_3PO_4 and a mixture of ethylene carbonate(EC), -butyrolactone(BL) and dimethylcarbonate (DMC) were examined in order to obtain the best compromise between high protonic conductivity, homogeniety and dimensional stability. Measurements of differential scanning calorimetry and ionic conductivity have been carried out for various compositions. The highest proton conductivity of 7.3×10^{-3} Scm⁻¹ at 30 were obtained for a film of $30(PVdF-HFP) + 50EC/DMC + 20H_3PO_4$. From the thermal study, it has been found that the PVdF-HFP gels are stable up to 80 , and the H_3PO_4 enhances the miscibility of the polymer and the solvent by interacting sensitively with polymer segments.

Keywords: proton conductivity, proton conducting gel electrolyte, polymer electrolyte, PVdF-HFP.

```
가 .1.2
, polyelectrolyte - poly(acrylonitrile) (PAN), poly
hydrogel (methyl methacrylate) (PMMA) poly(vinyli-
```

26 2 2002 3 179

dene fluoride) (PVdF)		
Li- 가	, HFP	
 Li - H ₃ PO ₄ , H ₂ SO ₄	Shimadzu different calorimeter (TA - 50 WSI)	ial scanning
propylene carbonate(PC)	10 mg He	-
	- 130	
PC ethylene carbonate(EC) .		71
	-110 250 10 min ⁻¹	가
•	(HD m	nodal 4102A
		nodel 4192A
D\/dE	LF) .	- 4 MII-
- PVdF	100 Hz	z 1 MHz
FINIMA . Poly	7 7	•
(vinylidene fluoride - hexafluoropropylene) (PVdF - HFP)	Z Z	
. PVdF - HFP	Z .	
PVdF		
PVUP		•
,		
.8 PVdF - HFP EC		
- butyrolactone(BL) EC dimethyl	Figure 1 PVdF-HFP EC, BL	
carbonate(DMC) H ₃ PO ₄	EC/BL	DSC
-	. PVdF - HF	
,	T _g Figure 1 0	
,	. PVdF	T_g
		HFP *
	가	
PVdF - HFP (92 wt% PVdF 8 wt% HFP	PVdF - HFP 130	150
(Solvey)), H ₃ PO ₄ (99.999%	가 . PVdF HFP	
, Aldrich), EC, BL DMC , tetrahyd -	. PV	'dF
rofuran (THF)	T _m 171 , HFP가	
4 - (molecular sieve)		, PVdF
. 1:1 EC/BL EC/DMC	HFP T _g T _m	PVdF
H ₃ PO ₄ THF .	, ア	
60 PVdF - HFP	$T_g = T_m$	
	9	
Ar THF		
가 25 100 μm free-standing		
. PVdF - HFP 30 mol%	가	
	T _a 가 PVdF	- HFP

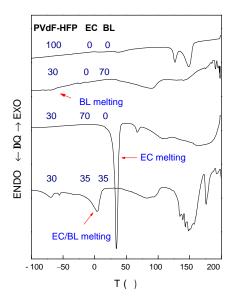
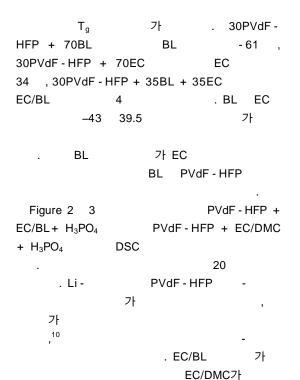
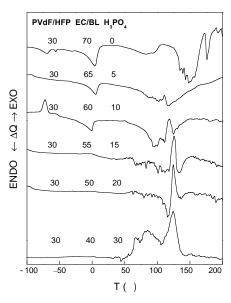


Figure 1. DSC thermograms of PVdF - HFP polymer and PVdF - HFP + EC/BL gels.







 $\begin{aligned} & \textbf{Figure 2.} & \ \, \text{DSC thermograms of PVdF-HFP} \, + \, \text{EC/BL} \\ & + \, \, \text{H}_{3}\text{PO}_{4} \, \text{proton conducting gel electrolytes}. \end{aligned}$

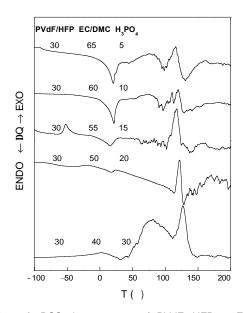


Figure 3. DSC thermograms of PVdF-HFP + EC/DMC + $\rm H_3PO_4$ proton conducting gel electrolytes.

가

가

EC/BL

	- 가	PVdF/HFP EC/BL H ₃ PO ₄	
가	,	-1.5 - 30 65 5 ■ 30 60 10	
	. ^{11,12} 120 -	_	
140		-2.0	
가	가 .		
200	·		
DSC		E -2.5 9) b	
200		0	
•	80	O -3.0	
	80		
	DV 15/115D 0050/DI	25	
=	PVdF/HFP + 60EC/BL +	-3.5	
10H ₃ PO ₄ Figure 3	30PVdF/HFP + 55EC/		
DMC + 15H ₃ PO ₄	- 60	-4.0 3.0 3.1 3.2 3.3 3.4 3.5 3.6	
- 50	가 .	1000/T (K ⁻¹)	
10	20	·	
가	EC	Figure 4. Temperature dependence of the ionic conductivity of PVdF - HFP + EC/BL + H ₃ PO ₄ proton	
		conductivity of Fvar - HFF + EC/BL + H ₃ FO ₄ proton conducting gel electrolytes.	
	가	conducting ger electrorytes.	
		가 가	
	가		
	·	가	
		DSC	
quenching /		가 .	
quenoi		Figure 4 5 PVdF-HFP + EC/BL + H ₃ PO ₄	
, 가		_	
	quenching	PVdF - HFP + EC/DMC + H ₃ PO ₄	
가	가		
	quenching	. PVdF - HFP	
EC	가		
가	가	. EC/BL	
	가	30(PVdF-HFP) + 55EC/BL +	
		15H ₃ PO ₄ 6.0×10 ⁻³ Scm ⁻¹ 가	
		, EC/DMC 30	
EC가	가 .	(PVdF-HFP) + 50EC/DMC + 20H ₃ PO ₄	
quenching	· · · · · · · · · · · · · · · · · · ·		
가	가	가 가 가 가	
•			
		Figure 6 30	
가	, quanching	. PVdF - HFP	
∕ r	quenching	. FVUF-NFF	
,			
가	quenching	. EC,	

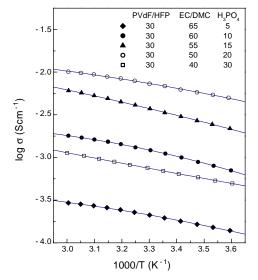


Figure 5. Temperature dependence of the ionic conductivity of PVdF-HFP + EC/DMC + H_3PO_4 proton conducting gel electrolytes.

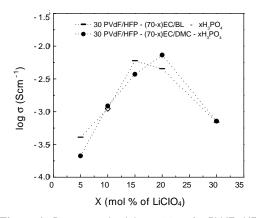
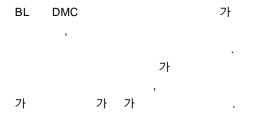
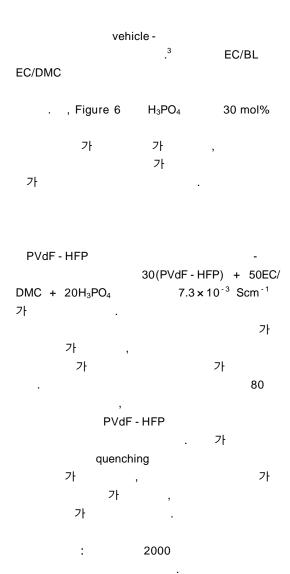


Figure. 6. Proton conductivity at 30 for PVdF - HFP + EC/BL + H_3PO_4 and PVdF - HFP + EC/DMC + H_3PO_4 proton conducting gel electrolytes fixed with 30 mol% of PVdF - HFP.





- J.C. Lasseques in "Proton Conductors: Solids, Membranes and Gel - Materials and Devices", ed. by Ph. Colomban, ch. 20, Cambridge University, Cambridge, 1992.
- 2. K.D. Kreur, Chem. Mater., 8, 610(1996).
- D. Raducha, W. Wieczrok, Z. Florjanczyk, and J. R. Stevens, J. Phys. Chem., 326, 20126(1996).
- 4. W. Wieczorek and J. R. Stevens, *Polymer*, 38, 2057 (1997).

- 5. S. Panero and B. Scrosati, *J. Power Sources*, 90, 13(2000).
- W. Wieczorek, G. Zukowska, R. Borkowska, S. H. Chung, and S. Greenbaum, *Electrochim. Acta*, 46, 1427(2001).
- F. Gray and M. Armand, in "Handbook of Battery Materials", ed. by J.O. Besenhard, part , ch. 8, Wiley - VCH, 1999 and references therein.
- A. S. Gozdz, J. M. Tarascon. O. S. Gebizlioglu, C. N. Schmutz, P.C. Warren, and F. K. Shokoohi, in "Rechargeable Li and Li ion Batteries", eds. by

- S. Megahed, B. M. Barnett and L. Xie, Electrochem. Soc., Pennington, 1995.
- 9. R. G. Beeman, J. Polym. Sci., 9, 472(1953).
- 10. Y. W. Kim, M. S. Gong, and B. K. Choi, *J. Power Sources*, 97 98, 654(2001)
- 11. K. Hayamizu, Y. Aihara, S. Arai, and W. Price, *Solid State Ionics*, 107, 1(1998).
- S. Abbrent, J. Plestil, D. Hlavata, J. Lindgren, J. Tegenfeldt, and Å. Wendsjö, *Polymer*, 42, 1407 (2001).