



ELSEVIER

Journal of Power Sources 97–98 (2001) 649–653

JOURNAL OF  
**POWER  
SOURCES**

www.elsevier.com/locate/jpowsour

# Preparation of microporous PVDF based polymer electrolytes

Haitao Huang, Stephanie L. Wunder\*

*Department of Chemistry, Temple University, Philadelphia, PA 19122, USA*

Received 2 June 2000; accepted 4 December 2000

## Abstract

Microporous PVDF-HFP (Kynar 2801) and PVDF-HFP/PS (where PS is polystyrene) films were prepared without solvent extraction using a solvent/nonsolvent method and the volatile plasticizers propyl carbonate (PC) or diethylcarbonate (DEC). Films with and without silicon dioxide ( $\text{SiO}_2$ ) were prepared. The conductivity of the films increased with increasing pore volume, measured by a nonsolvent uptake method. The films had improved conductivity compared with films made using the Bellcore process. Conductivities of  $4 \text{ mS cm}^{-1}$  were obtained using the liquid electrolyte  $\text{LiPF}_6$  (1 M) in EC/DMC/DEC (4:5:1 by weight). © 2001 Published by Elsevier Science B.V.

*Keywords:* Microporous PVDF; Diethylcarbonate; Bellcore process

## 1. Introduction

Extraction of the plasticizer from PVDF-HFP/ $\text{SiO}_2$  polymer electrolytes is a widely used method called the Bellcore process that results in a nanoporous morphology [1]. It has been reported that increasing the pore size (e.g. to micron size) in the PVDF matrix can help to enhance the ionic conductivity and thus improve cell rate capability [2–7]. The improvements observed in the trend from gel to nanoporous to microporous PVDF based polymer electrolytes suggests that control of the phase morphology of the pore structure, and understanding the relationship between this structure and cell performance, will be critical for future improvements in these systems.

To prepare microporous films, Pasquier and coworkers at Telcordia Technologies (formerly Bellcore) have reported an extractionless process using a volatile plasticizer, dimethyl phthalate (DMP) [6,7], and Boudin and coworkers at SAFT proposed preparing PVDF homopolymer films using a phase inversion process with a solvent/nonsolvent system [4,5]. In our previous work [2,3], we reported the formation of microporous PVDF-HFP films using PEO oligomers instead of dibutyl phthalate (DBP). These films had improved conductivity compared with films made using the Bellcore process. In this work, we further explore the ways to produce microporous PVDF-HFP films, with and

without  $\text{SiO}_2$ , with high conductivity and good mechanical strength. Films are prepared with and without solvent extraction, using a solvent/nonsolvent system and/or a volatile plasticizer. Since the phase separation behavior has been described as a spinodal decomposition process, the development of structure will be time dependent. For a given solution, the volatility of the components of the cast films will affect phase separation and thus the film porosity. In addition, this method has been applied to prepare novel microporous films of PVDF-HFP blended with polystyrene (PS), with and without  $\text{SiO}_2$ . Films with a range of porosities were prepared and the pore structure of the PVDF-HFP/PS without  $\text{SiO}_2$  was characterized using a nonsolvent absorption method (to measure pore volume) and  $\text{N}_2/\text{He}$  adsorption using the BET technique (to measure pore surface area). The ionic conductivity was found to correlate with increasing pore volume.

## 2. Experimental

The PVDF-HFP (KYNAR 2801, ELF Atochem), propylene carbonate (PC) or dimethyl carbonate (DMC) and hydrophobic (silanated with hexamethyldisilazane) fumed silica (Cabosil TS530,  $\sim 12 \text{ nm}$  primary particle size) were mixed in an acetone/alcohol mixture. Acetone is a solvent for PVDF, and PC and DMC are also soluble in the amorphous phase of PVDF-HFP. The alcohols used were butanol (BuOH), ethanol (EtOH) or methanol (MeOH), and all are nonsolvents for PVDF, but dissolve PC and DMC and are

\* Corresponding author.

E-mail address: slwunder@unix.temple.edu (S.L. Wunder).

miscible in all proportions with acetone. Slurries consisting of 30% PVDF-HFP, 20% fumed  $\text{SiO}_2$  and 50% plasticizer, were mixed in the acetone/alcohol mixture. The resulting slurry was doctorbladed onto a polyester sheet. After evaporation of the acetone/alcohol, strong, self-supporting thin films were formed. The PC or DMC plasticizer was removed through evaporation under vacuum or atmospheric pressure at room temperature.

The PVDF-HFP/PS blend polymer films were prepared by first mixing solutions of PVDF-HFP (KYNAR 2801 and 2750, ELF Atochem) in acetone and PS (Aldrich) in DMC. PS is not soluble in acetone, but dissolves in DMC at  $\sim 50^\circ\text{C}$ . A fine precipitate, which was kept in suspension by constant agitation, formed when the solutions were mixed. Butanol was added to the PVDF-HFP/PS mixture and films were cast in the same manner as described above. In some cases, fumed  $\text{SiO}_2$  was added to the PVDF-HFP/PS polymer mixture before films were cast. Information about the preparation procedure will be discussed in detail elsewhere. The polymer films were soaked in an electrolyte solution containing  $1 \text{ mol dm}^{-3}$  of  $\text{LiPF}_6$  dissolved in ethylene carbonate (EC)/DMC/DEC in the ratio 4:5:1 w/w/w. The films were then sandwiched between two stainless steel electrodes, and ionic conductivities were measured using ac impedance spectroscopy.

Cross-sectional views of the morphology of the films were observed using scanning electron microscopy (SEM) (Phillips SEM Model 501B). Specific surface area measurements were made using a single point BET technique (MONOSORS Surface Area Analyzer, Model MS-12, Quanta Chrome Co.) with  $\text{N}_2/\text{He}$  as the adsorbing gas. Pore volumes of the films were measured by uptake of a nonsolvent (BuOH) for the polymers.

### 3. Results and discussions

#### 3.1. Formation of microporous PVDF-HFP/ $\text{SiO}_2$ films

Fig. 1 is the SEM micrograph (magnification:  $2500\times$ ) of a PVDF-HFP/PC/ $\text{SiO}_2$  film prepared from a casting solution of 75 wt.% acetone and 25 wt.% butanol, clearly showing a microporous structure. Films prepared using the Bellcore process (PVDF-HFP/DBP/ $\text{SiO}_2$  using a single casting solvent) show no visible pore structure at this magnification [2]. When the nonsolvents methanol and ethanol are used in the casting solution in the same weight ratio with acetone, microporous films are also formed. The pores formed when methanol is used are slightly smaller than for ethanol or butanol. Strong, self-supporting films were formed except when the weight percent of nonsolvent (BuOH) exceeded 40%, when the films prepared were brittle and cracked easily.

The formation of a porous structure is a complex process that depends on the interactions of the solvents and plasticizers with the polymer/ $\text{SiO}_2$  and is kinetically controlled by the relative rates of evaporation of the components. For the systems investigated here, the plasticizers PC and DMC are both soluble in PVDF-HFP, but DMC is more volatile (bp  $90^\circ\text{C}$ ) than PC (bp  $240^\circ\text{C}$ ). If plasticizers are not used, the films shrink after solvent evaporation when  $\text{SiO}_2$  is present. The alcohols (BuOH, EtOH and MeOH) are nonsolvents for PVDF-HFP, and have boiling points of 118, 78 and  $65^\circ\text{C}$ , respectively; acetone boils at  $56^\circ\text{C}$ . Although the volatility of a compound is not the same as the boiling point, the latter will be assumed to follow the same trends expected for the former.

As the acetone evaporates, the solution becomes richer in nonsolvent, and the polymer precipitates in the nonsolvent

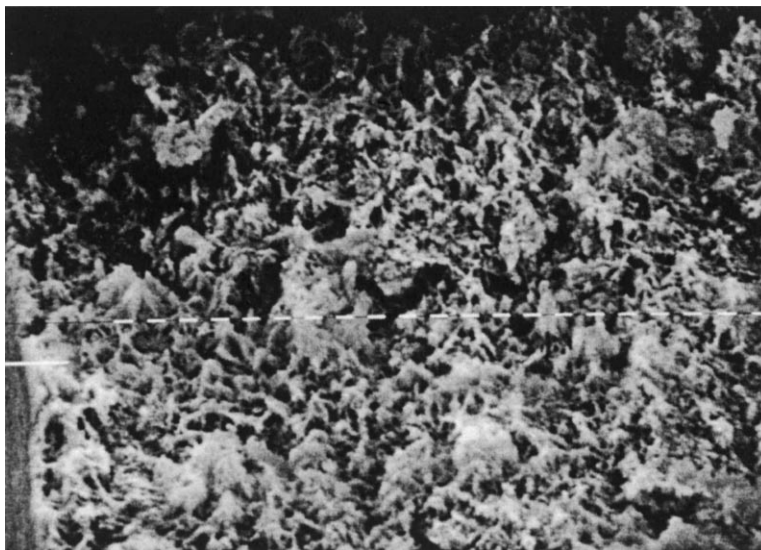


Fig. 1. SEM of the cross-section of the PVDF-HFP/ $\text{SiO}_2$  film prepared using PC plasticizer and cast from acetone/BuOH mixture. PC was removed by evaporation (the short bars in the graph represent 1 mm).

phase, resulting in void formation in the polymer matrix after evaporation of the nonsolvent. When PC is used as the plasticizer, evaporation of the solvent/nonsolvent precedes removal of the PC, and void formation is controlled by the relative rates of evaporation of the solvent/nonsolvent. Since the bp of MeOH is only slightly above that of acetone, the existence of the nonsolvent phase, and thus the time evolution of structure development is short compared with EtOH and BuOH. This may explain the smaller pore size observed in films prepared using PC/MeOH compared with PC/EtOH or PC/BuOH. Ionic conductivity ( $\sigma$ ) measurements, discussed below (Fig. 2), indicate that  $\sigma$  of films prepared with PC/EtOH or PC/BuOH are greater than those prepared using PC/MeOH.

When the solvent/nonsolvent is kept constant, e.g. for acetone/butanol, and the plasticizer is varied, similar trends are observed. The acetone is removed first, leaving BuOH/PC or BuOH/DMC. In the former case, the nonsolvent BuOH evaporates first, leaving the soluble plasticizer. In the latter case, the solvent DMC evaporates more quickly than the nonsolvent BuOH, allowing a longer time for development of the phase separation process. Films prepared using PC or DMC both exhibit a microporous morphology, but quantitative differences between them have not yet been obtained. Ionic conductivity measurements, given below (Fig. 2), indicate that the  $\sigma$  of BuOH/DMC films is greater than  $\sigma$  of BuOH/PC films.

### 3.2. Formation of microporous PVDF-HFP/PS and PVDF-HFP/PS/SiO<sub>2</sub> films

Microporous films were formed when mixtures of PVDF-HFP and PS, with and without the addition of fumed silica, were cast from acetone/BuOH/DMC solutions. Microporous structures (at 2500× magnification by SEM) were not observed for films cast from acetone/DMC, nor for films prepared without PS (in absence of SiO<sub>2</sub>). Tough, strong, self-supporting films were formed when PS contents of up to

40% were used for film formation; films with increased concentrations of PS have not yet been prepared. Fig. 3 presents the micrographs of PVDF-HFP/PS blend films, containing 10, 20 and 30% of PS, respectively, prepared in the presence of butanol. Pores greater than 0.5 μm were formed, and the porosity increased with increasing content of PS. Ionic conductivity measurements (Fig. 2) showed that  $\sigma$  increased with increasing PS content. Conductivity also

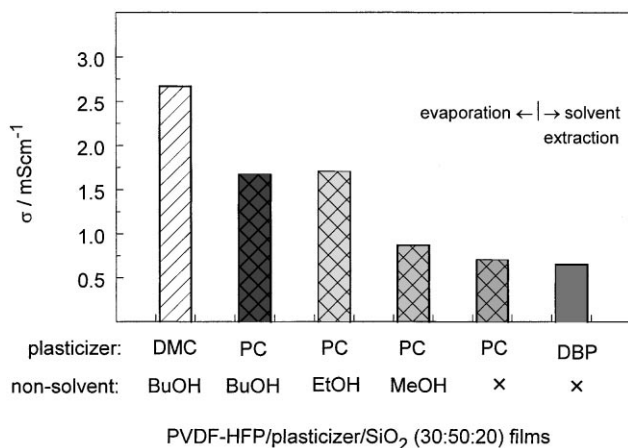


Fig. 2. Conductivities of PVDF-HFP/plasticizer/SiO<sub>2</sub> (30:50:20 w/w/w) polymer films soaked with the electrolyte of 1 M LiPF<sub>6</sub>/EC/DMC/DEC.

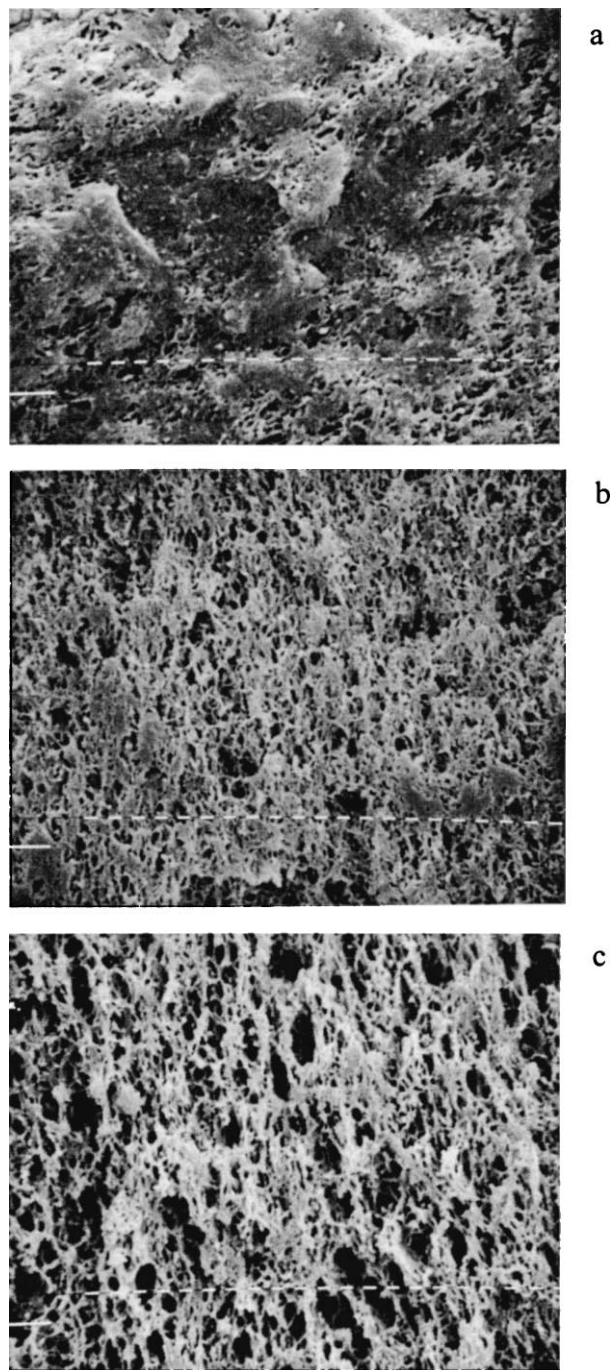


Fig. 3. SEM of the cross-sections of the PVDF-HFP/PS blend polymer films: (a) 10% PS; (b) 20% PS; (c) 30% PS (the short bars in the graphs represent 1 mm).

increased with addition of fumed silica. Since butanol is nonsolvent for both PVDF and PS, a similar phase separation mechanism as discussed above may occur for the PVDF-HFP/PS system.

### 3.3. Ionic conductivity

A mechanism consisting of two conduction paths has been postulated in the case of gel polymer electrolytes [8,9]. The effective higher conductivity pathway decreases with increasing polymer content. In the case of porous polymer electrolytes, the microporous matrix is believed to help enhance conductivity because liquid electrolyte is trapped in the pores [4]. If the microporous structure were really a two phase system, there would be only a single high conductivity path consisting of the liquid phase; the polymer structure would only provide a rigid support. Conductivity would be expected to increase with increasing pore volume. However, in the microporous networks, swelling of the pore walls is expected because of the compatibility of the solvent and the polymer. With increasing amount of PS in a PVDF-HFP/PS blend, the swelling is expected to decrease. For a given weight fraction of polymer, and the same electrolyte uptake, the conductivity is thus expected to be higher for the film with the greater weight percent PS.

The results of the conductivity measurements from PVDF-HFP/SiO<sub>2</sub> films given in Fig. 2 verify the importance of micropore volume to ionic conductivity. The conductivity of a film prepared using the Bellcore process is included for comparison. Similarly, a PVDF-HFP/SiO<sub>2</sub> film prepared using PC as plasticizer but without BuOH in the casting solvent, had a low conductivity (0.7 mS cm<sup>-1</sup>). In marked contrast, the films that possess a microporous network, as indicated by SEM, show high conductivity. For example, the film prepared using acetone/BuOH/DMC exhibits a conductivity of 2.5 mS cm<sup>-1</sup>.

The results of conductivity measurements for PVDF-HFP/PS blend polymer films are given in Fig. 4, and the result for a PVDF-HFP/PS film prepared without the use of butanol is included. The latter has a nonmicroporous struc-

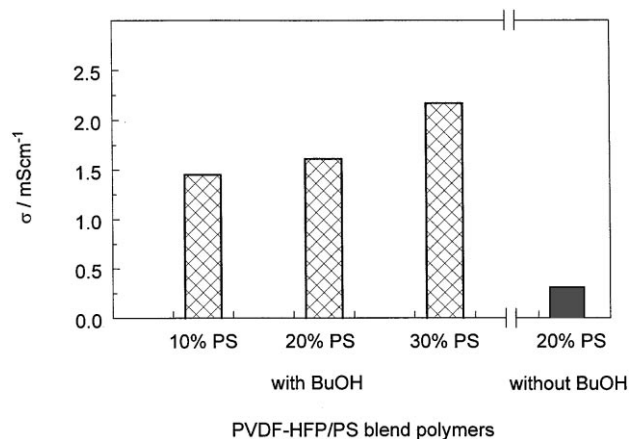


Fig. 4. Conductivities of PVDF-HFP/PS blend polymer films soaked with the electrolyte of 1 M LiPF<sub>6</sub>/EC/DMC/DEC.

ture (by SEM) and poor conductivity (0.3 mS cm<sup>-1</sup>). The conductivity of microporous PVDF-HFP/PS films increase with increasing PS content and approach 2.1 mS cm<sup>-1</sup>. As will be discussed in detail later, the electrolyte uptake is similar for these samples. This suggests that with increasing PS content, less of the electrolyte swells the pores. Addition of fumed SiO<sub>2</sub> into the PVDF-HFP/PS system further raises the conductivity to nearly 4 mS cm<sup>-1</sup>.

### 3.4. Characterization of pores

The PVDF-HFP/PS blend polymers in Fig. 4 were subjected to further characterization. First, BuOH uptake by the films was examined. Since PVDF-HFP and PS do not swell in BuOH, any increase in the weight of the films after immersion reflects the solvent trapped in the pores. Therefore, BuOH uptake may be taken as a measure of porosity. The results given in Fig. 5 (solid circles, and connected by a line for clarity) show that uptake of butanol positively correlates with increasing conductivity. The solid triangles in Fig. 5 (connected by a line for clarity) are the BET results. The BET data do not correlate well with the variation in the s

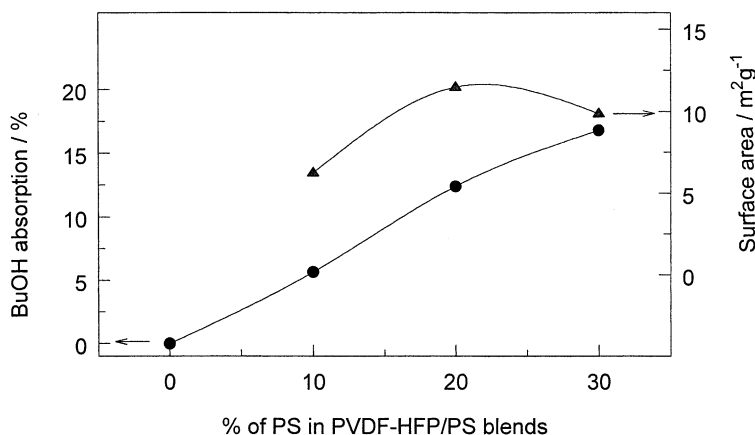


Fig. 5. BuOH absorption and surface area measurements of the films in Fig. 4.

suggesting that pore size and shape may need to be taken into account when using surface area as a measure of porosity. More detailed investigations are underway.

#### 4. Conclusions

Microporous PVDF-HFP based polymer films can be prepared without a solvent extraction method using a solvent/nonsolvent mixture when PC or DMC (instead of DBP) are used as plasticizers. PC and DMC aid in forming films that do not crack and can be easily removed under evaporation even at room temperature. The low bp of DMC may further help to increase the porosity of films, and thus increase conductivity. A new type of microporous film can be simply prepared based on PVDF-HFP blended with PS at the presence of the nonsolvent BuOH and added plasticizer. The porosity of the films increases with increasing amount of PS, providing an approach to study of the correlation of porosity to ionic conductivity. The BET method was used to study porosity from the point of surface area measurements, but pore size and shape have to be taken into account. Nonsolvent (BuOH) uptake by the polymer films gives a simple and straightforward way to determine pore volume within the polymer matrix.

#### Acknowledgements

We would like to thank Lithium Technology Corporation for supplying the liquid electrolytes, fumed silica, and the KYNAR polymer, and Dr. Grandstaff in the Department of Geology at Temple University for use of the BET instrument.

#### References

- [1] J.M. Tarascon, A.S. Gozdz, C.N. Schmutz, F. Shokoohi, P.C. Warren, *Solid State Ionics* 86/88 (1996) 49.
- [2] H. Wang, H. Huang, S.L. Wunder, *J. Electrochem. Soc.*, in press.
- [3] H. Wang, J.B. Kejha, Y.K. Yarovoy, S.L. Wunder, *Mater. Res. Soc. Symp. Proc.* 548 (1999) 347.
- [4] F. Boudin, X. Andrieu, C. Jehoulet, I.I. Olsen, *J. Power Sources* 81/82 (1999) 804.
- [5] X. Andrieu, C. Jehoulet, F. Boudin, I.I. Olsen, in: *Proceedings of the 38th Power Sources Conference, 1998*, p. 266.
- [6] A. Du Pasquier, P.C. Warren, D. Culver, A.S. Gozdz, G.G. Amatucci, J.M. Tarascon.
- [7] A. Du Pasquier, A.S. Gozdz.
- [8] A.M. Christie, L. Christie, C.A. Vincent, *J. Power Sources* 74 (1998) 77.
- [9] O. Bohnke, G. Frand, M. Rezzazzi, C. Rousselot, C. Truche, *Solid State Ionics* 66 (1993) 105.