

# Synthesis, Characterization and Electrochemical Properties of PVDF-HFP-g-PMMA Gel Electrolytes

J. Y. Lee<sup>1</sup>, Y. Liu<sup>1</sup> and L. Hong<sup>1</sup>

<sup>1</sup> Department of Chemical & Environmental Engineering  
National University of Singapore  
10 Kent Ridge Crescent, Singapore 119260

## Introduction

Among the polymers that can be used as the matrix for gel type electrolytes, the poly(vinylidene difluoride-hexafluoropropylene) (PVDF-HFP) copolymer has been the most comprehensively investigated [1]. Other polymer systems based on blending of polyethylene, polystyrene or poly(ethylene oxide) with PVDF-HFP have also been introduced. Here we report the synthesis of PVDF-HFP main chains with chemically grafted poly(methyl methacrylate) (PMMA) units to produce “polymer blends” at the molecular level and investigate the suitability of the product as a gel polymer electrolyte.

## Experimental

PVDF-HFP was pretreated by ozone before the thermally induced graft copolymerization. The product was dissolved in NMP and precipitated in ethanol to remove un-reacted monomer and homopolymers. The resultant PVDF-HFP-g-PMMA copolymer was characterized by FTIR, XPS, TGA and elemental analysis by a CHN analyzer. Gel type electrolytes based on this new PVDF-HFP-g-PMMA copolymer were prepared according to the Bellcore method [2]. The Li-polymer interfacial stabilities of these gel electrolytes were evaluated by monitoring the temporal changes in the impedance of symmetric Li/gel electrolyte/Li test cells under open-circuit conditions.

## Results and discussion

FTIR measurements confirmed the success of graft copolymerization. The spectrum of PVDF-HFP-g-PMMA in Fig 1(b) contains the characteristic band for O-C=O stretch ( $\nu = 1729 \text{ cm}^{-1}$ ), attributed to the ester groups in the PMMA grafted side chains. Figure 2 shows the TGA responses from both PVDF-HFP and PVDF-HFP-g-PMMA. For the PVDF-HFP sample, only a single weight loss event took place starting at around 420°C, which could be attributed to the decomposition of PVDF-HFP units by random scission. For the PVDF-HFP-g-PMMA sample, there were two additional weight loss events, starting at about 150°C and 370°C respectively. The first event could correspond to degradations initiated by the breaking of weak PMMA head-to-head linkages, and the second event was the result of random scission of the PMMA side chains [3]. The weight loss due to

the decomposition of the PMMA component was about 8-9% (w/w), in good agreement with the data from elemental analysis (8.5% w/w).

From the plot of Li-polymer interfacial resistance against time in Figure 3, the PVDF-HFP-g-PMMA based system is an enhancement over the PVDF-HFP system. The former had near invariant  $R_i$  values except for some slight fluctuations after the first 50 hours. The stability of the new gel polymer electrolyte was probably due to the excellent stability of the PMMA component in the copolymer, and the ability of the PMMA component to scavenge impurities and residue moisture within the gel system.

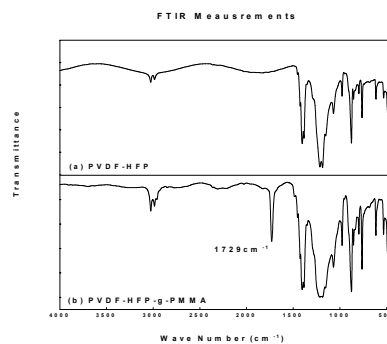


Figure 1 FTIR measurements

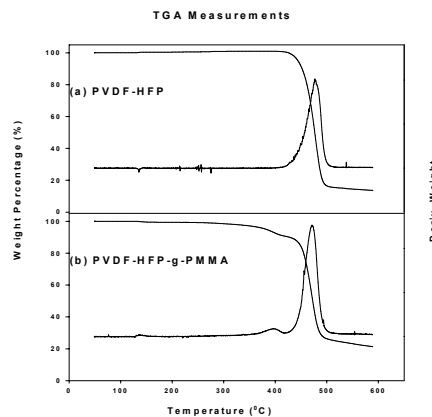


Figure 2 TGA measurements

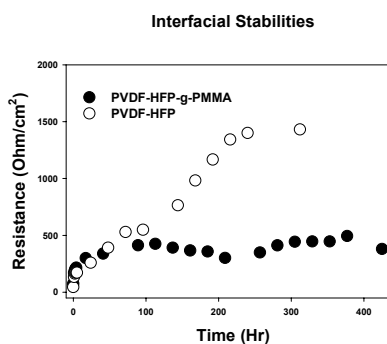


Figure 3 Stability of the Li/gel electrolyte interface

## References

- [1] J.Y. Song, Y.Y. Song and C.C. Wang, *J. Electrochem. Soc.*, 147 (9), **2000**,3219
- [2] T. Gozdz, C. Schmutz, J. M. Tarascon, P. Warren, *US Patent No. 5,418,091*
- [3] M. Cochez, M.Ferriol, J.V. Weber, P.Chaudron, N.Oget and J.L. Mieloszynski, *Polymer Degradation and Stability*, 70, **2000**, 455