"Effect of Fumed Silica on Mechanical Properties and Ionic Conductivity of PMMA Gel Electrolytes"

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Amorphous pyrogenic (fumed) silica has been used in composite polymer electrolytes for lithium rechargeable batteries for a variety of reasons, including the stability of the interface and suppression of PEO crystallinity. In more recent studies, it was also demonstrated that incorporation of fumed silica or surface-modified fumed silica to a continuous phase of a low molecular weight oligomeric polyether may result in a material with both good mechanical stability and high ionic conductivity.

Previously, we have reported on a new stereocomplexed PMMA rubber-like gel electrolyte exhibiting ionic conductivity in the range from 1 to 4 mS/cm at room temperature and tensile moduli in excess of 1×10^5 Pa. Our objective in this study is to determine whether fumed silica may further improve mechanical and conductive properties of gel electrolytes based on stereocomplexed PMMA.

We have tested several commercially available fumed silicas with different surface groups, particle sizes and areas, whose properties are presented in Table I. The electrolyte formulations and their mechanical properties are presented in Table II. For both electrolye systems, [PC/$LiCF_3SO_3$ or EC:DMC:EMC/$LiPF_6$] replacement of PMMA with fumed silica at constant total (20) wt% (PMMA + SiO_2) resulted in an increase from between 23% to 45% in the storage moduli when compared with the corresponding nonfiller system. the largest increase in storage modulus, 45% compared with unfilled gels, was observed for the fumed silica with the highest surface area, A380.

In order to increase the association between silica and PMMA, we synthesized a glass-polymer composite, by first silanating A380 fumed silica with 3-(trimethoxysily)propyl methacrylate (MtPS). Methyl methacrylate monomer was then polymerized in the presence of the methacrylate functionalized silica. The amount of PMMA covalently attached to the silica, its stereoregularity and molecular weight were characterized by thermogravimetric analysis (TGA), NMR and gel permeation chromatography (GPC). The noncovalently bonded PMMA was solvent extracted, and the bound PMMA was removed from the silica using HF. The stereocomplexes PMMA gels formed using the PMMA-SiO_2 composite material had the best mechanical properties, while maintaining the same ionic conductivity.

A modulus versus temperature curve for gels with 1.3% A380 is shown in Figure 1. Mechanical properties are maintained to temperatures about 10^{o}C higher than gels without silica or gels prepared using physical mixtures of fumed silica.

Table I. Physical properties of fumed silica

Fumed Silica	Particle Size (nm)	BET surface area(m^2/g)	Surface Groups
Aerosil 200	12	200 ± 25	SiOH
Aerosil 380	7	380 ± 30	SiOH
Aerosil R972	16	110 ± 20	$-CH_3$
Aerosil R805	12	150 ± 25	$-(CH_2)_7CH_3$

Table II. Composition and storage moduli of PMMA based electrolytes with and without fumed silica

PMMA wt%	Silica type	Solvent	Salt (1M)	Storage moduli (10^4Pa)
20	0	PC	$LiCF_3SO_3$	12.1
17	A200,3%	PC	$LiCF_3SO_3$	14.9
17	R805,3%	PC	$LiCF_3SO_3$	16.4
17	A380,3%	PC	$LiCF_3SO_3$	17.5
20	0	EC:DMC:EMC (1:1:1)	$LiPF_6$	3.2
17	R972,3%	EC:DMC:EMC (1:1:1)	$LiPF_6$	5.7

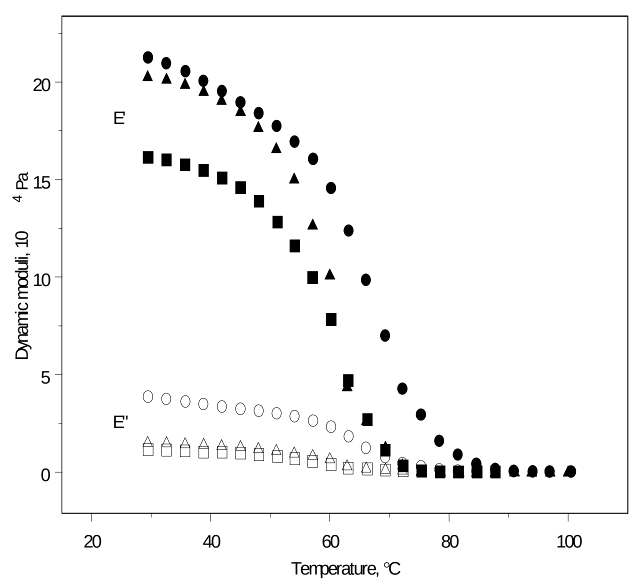

Fig. 1. Temperature dependence of dynamic moduli of gel electrolytes based on PMMA and fumed silica in $LiCF_3SO_3$/PC system. (■) Without fumed silica, (▲) With fumed silica A380 (1.3%), (●) With PMMA grafted A380 (1.3%). Upper curves: storage moduli, E'; lower curves: loss moduli, E". Test frequency: 1 Hz.