

**COMPOSITE POLYMER ELECTROLYTES FOR
Li BATTERIES: ENHANCEMENT OF
PROPERTIES DUE TO MODIFICATION OF THE
INORGANIC COMPONENT**

L.M. Bronstein, R. Karlinsey, K. Ritter, C. Joo,
E. Ashcraft, and J. W. Zwanziger
Indiana University, Chemistry Department
Bloomington, IN 47405

Recently, composite polymer electrolytes consisting of polymer-in-salt together with inorganic components have drawn the attention of several research groups, as these materials display a number of advantages compared to simple polymer-in-salt electrolytes. Advantages of these composite materials include the ability to suppress PEO crystallization and the enhancement of mechanical properties. In many cases, composite electrolytes also show much higher conductivity and Li transference numbers, which are crucial for successful application in Li batteries. Among inorganic components incorporated in composite polymer electrolytes, the most popular are inorganic fillers (Al_2O_3 , SiO_2 , TiO_2 etc.), with particle sizes varying from microns to nanometers [1,2]. In another approach, composite materials including clay platelets displayed strongly modified properties with very weak temperature dependence of conductivity, but rather low conductivity at room temperature [3].

The more general option for development of composite materials with an inorganic component is realized when the latter forms *in situ* within the polymer matrix [4,5]. In this case, depending on reaction conditions and the ratio of organic to inorganic components, both nanoparticles and interpenetrating networks can be obtained. As reported by us recently [5], the sol-gel reaction of aluminum tri-*sec*-butoxide and (3-glycidyl-oxypropyl)trimethoxysilane (GLYMO) in 'PEO+Li triflate' medium results in interpenetrating an aluminosilica network when 8,000 MW PEO and 70% inorganic component are used.

Table 1 shows the conductivity of these composite materials derived from 600 MW PEO. One can see that conductivity decreases as the amount of inorganic component increases, which implies a corresponding decrease of the amount of Li ions in the system and related decrease of the material dielectric constant. An important advantage of this composite material is the easy modification of its structure. Partial replacement of one of the components of the inorganic part for the precursor containing a functional group can influence the dielectric constant and/or reactivity of the inorganic part. In this paper we report on incorporation of silane-containing CN groups (2-cyanoethyltrimethoxysilane), which was expected to increase the dielectric constant of the composite polymer electrolyte. As can be seen from Fig. 1, the room temperature conductivity is strongly influenced by incorporation of CN groups tethered to aluminosilica (CN modifier partially replaces GLYMO); however this influence depends on the overall amount of inorganic component and quantity of CN modifier. On the other hand, increase of conductivity is not accompanied by the increase of dielectric constant (Table 1). As GLYMO is replaced by the CN modifier, the overall crosslinking density of the inorganic network partially provided by the epoxy rings of GLYMO changes, and thus the interface between 'PEO+Li triflate' and inorganic component changes as well, which can cause the increase of conductivity. Variable temperature data presented in Fig. 2 and activation energies derived from them (Table

1) show lower temperature dependence of conductivity than for pure 'PEO+Li salt' electrolyte [6] which confirms interaction of aluminosilica with Li ions.

References

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Table 1. Room temperature conductivity, activation energy (E_a) of conductivity, and dielectric constants for composite polymer electrolytes based on regular aluminosilica (L6-40, L60-55, and L6-70) and CN-modified aluminosilica.

sample notation	r.t. cond., S/cm	E_a , kJ/mol	dielectric constant
L6-40	2.90E-05	68.1	29
L6-55	1.35E-05	64.4	17
L6-70	1.77E-06	54.4	12
L6-40CN(37.5 mol.%)	6.10E-05	68.2	24

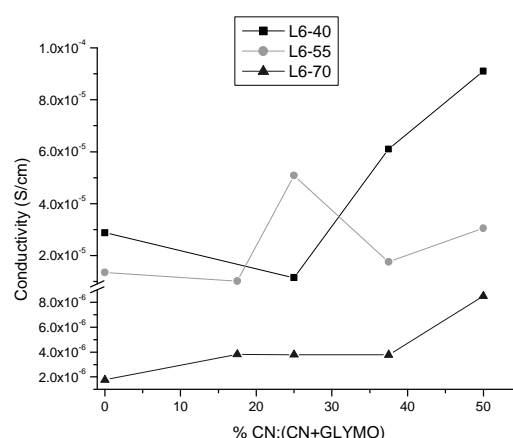


Fig. 1. 20 °C -conductivity data for 600 MW PEO samples with 40, 55, and 70 wt.% inorganic component and varying concentrations of CN modifier.

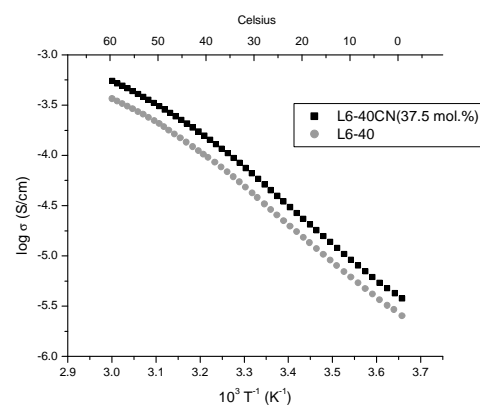


Fig. 2. Variable temperature data for 600 MW PEO samples with 40 wt.% inorganic component with, and without, CN modifier.