

New Inorganic-Organic Polymer Electrolytes based on Polyethylene Glycol 400 and Aluminum Isopropoxide: Synthesis and Structural Characterization (part I).

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Great effort is currently directed toward hybrid inorganic-organic systems in order to improve the performances of lithium ion conducting materials devoted to reversible energy storage^[1,2]. Classic polymer electrolytes are based on polyethylene oxide matrices doped with low dissociation energy lithium salts^[1,2]. Two very promising approaches were proposed so far to overcome the limitations of classic lithium polymer electrolytes and two main categories of hybrids were obtained. The first class is represented by (nano)composite electrolytic complexes, named CPE (composite polymer electrolyte)^[3]. These systems consist of conventional polymer electrolytes containing inorganic species embedded in the host matrix. It was suggested that the inorganic species interfaced with the polymeric chains generate the “grain boundaries” effect which increases significantly the conductivity. The second main class consists in the materials synthesized by copolymerization of organic macromolecules with metal and non-metal alkoxides, the so-called ORMOCERS-APE (organically modified ceramics as polymer electrolytes)^[4-6]. Examples of three-dimensional network based on organic macromolecules bridged together by inorganic atoms like Ti, Zr and Si are known. In these systems the conductivity depends on the doping salt and the size of the coordination “nests” present in the material. Alternatively hybrid inorganic-organic polymer electrolytes containing “ate” complex structure (e.g. aluminate, borate, etc.) were also investigated^[7]. The incorporation of Lewis acid sites into the inorganic backbone facilitates the delocalization of anionic charge, the reduction of cation-anion pairing with an increase of ionic conductivity.

In this report, the preparation of eleven new aluminum containing ORMOCERS-APE materials is presented. The synthesis of each system was performed by reacting Aluminum isopropoxide and a PEG400/(LiClO₄)_x solution with $0 \leq x \leq 4.890 \cdot 10^{-1}$. The resulting products were transparent materials with solid rubbery consistency and with general formula $\{Al[(CH_2CH_2O)_{8.671}]_p/(LiClO_4)_z\}_n$ where $1.85 \leq p \leq 2.24$ and $0 \leq z \leq 1.06$.

The structural hypothesis (Fig. 1) for these systems is proposed on the basis of elemental analyses and vibrational results. Medium FT-IR and FT-Raman studies of the polymers showed that the polyether fragments exhibit a conformational geometry close to TGT (T = *trans*, G = *gauche*) and allowed us to investigate the polymer-polymer and salt-polymer interactions. Taken together, these results indicated also an unexpected “anion trapping” ability of the aluminum atoms toward perchlorate anions.

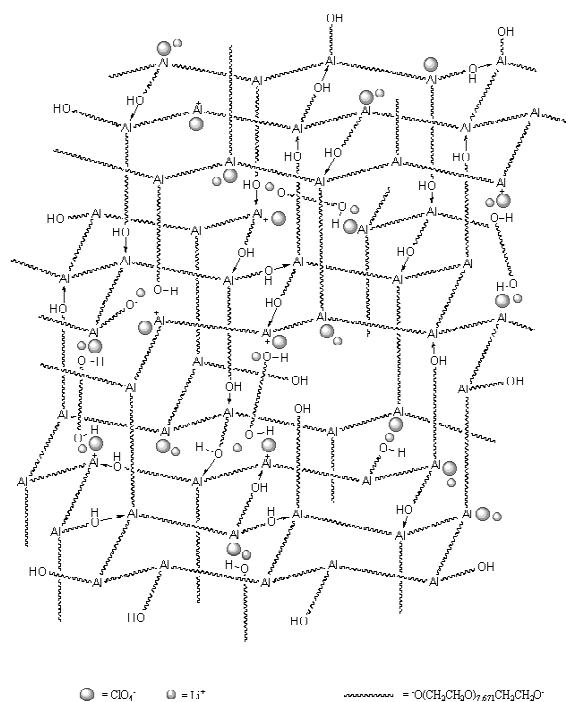


Fig. 1: Structural hypothesis proposed for the $\{Al[(CH_2CH_2O)_{8.671}]_p/(LiClO_4)_z\}_n$ electrolytic complexes.

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