NANOCOMPOSITE POLYMER ELECTROLYTES: EFFECT OF LAYER CHARGE ON THE INTERCALATION OF POLYETHYLENE OXIDE IN LAYERED SILICATES

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Polymer nanocomposites represent a radical alternative to conventional composite electrolytes. Of particular interest are Li salts dissolved in flexible polymers like polyethylene oxide (PEO). A serious drawback in these systems is the precipitous decrease in conductivity at temperatures below the melting temperature, which is typically above room temperature. One of the most promising ways to improve the electrochemical performance of polymer electrolytes is to form composite electrolytes by adding inorganic fillers.

Intercalation of PEO in layered hosts and in particular in layered silicates has been studied extensively. Based mostly on X-ray diffraction studies, there are two models: 1. The PEO adopts a helical structure inside the host galleries. The exchangeable cations reside inside the helix and are coordinated to the oxygen atoms of PEO. 2. The PEO chains are organised in an extended, all-trans bilayer parallel to the silicate surface.

The effect of layer charge on the intercalation of polyethylene oxide (PEO) was investigated using a series of reduced-charge montmorillonites and smectites with varying layer charge (fluorohectorite, saponite, three montmorillonite samples, nontronite and iron-rich beidellite).

Nanocomposites were prepared by solution or melt intercalation and using PEO of various molecular weights.

Melt or solution intercalation of PEO into layered silicates leads to essentially identical structure in the nanocomposite. The amount of intercalated polymer initially increases with layer charge but then decreases. In contrast the amount of water present after PEO adsorption continuously increases with layer charge. This is water mostly coordinated with the gallery cations. When PEO is intercalated it replaces water molecules filling the space between the hydrated exchangeable cations. No direct association between exchangeable cations and PEO oxygen atoms takes place. The amount of polymer adsorbed is controlled by the layer charge density, i.e. the surface area covered by the hydrated cations vs. surface covered by weakly adsorbed water. Molecular simulations confirm the experiments and show that the polymer oxygen atoms do not directly associate with the exchangeable cations, which are mostly coordinated to water molecules and surface oxygens atoms. The trends observed in this study may be applied to the intercalation-adsorption of layered silicates with other polymers or organic compounds.