

Functionalized Nanoparticle Silicas as Single Ion Conductors

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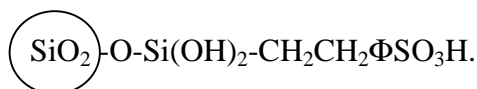
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The development of a solid polymer electrolyte with high ionic conductivity and cationic transport number as well as the requisite electrochemical stability, has been the subject of extensive recent research in secondary lithium and lithium ion batteries. Since the movement of the anions is not needed in the performance of the cell, and in fact contributes to deleterious polarization effects, the use of a single-ion conductor (SIC) is the solid electrolyte of choice. However, in a true SIC electrolyte, the composite electrodes must contain the single-ion conducting species in order to avoid high electrode-electrolyte impedance. Many organic and inorganic/organic polyelectrolytes have been investigated as SICs. The poor solubility of polyelectrolytes prevents their easy incorporation in the electrodes. In order to avoid this problem, we have investigated the preparation of cationically-functionalized nanoparticle-sized silica.

Two silica systems, namely high surface area pyrogenic fumed silica [Aerosil 380 (A380) from deGussa], with a nominal surface area of 380m²/g and primary particle size of 7nm, and polyhedral oligosilsequioxanes (POSS) have been investigated. POSS are nano-sized inorganic materials with a silica core and reactive functional groups on the surface. In the former case the silica surface contains silanol groups, Si_sOH, where Si_s is a surface silicon atom. It has been functionalized using the silanes 2-(4-chlorosulfonylphenyl) ethyl trimethoxysilane or 2-(4-chlorosulfonylphenyl) ethyl trichlorosilane to produce



In the latter case, octa(dimethylsiloxy)silsequioxane (Q₈M₈^H) containing reactive Si-H groups has been hydrosilylated with allyl-R, where R contains a cationic group, in the presence of platinum catalyst. In addition, both dimethylethoxysilane or dimethylchlorosilane have been reacted with A380, in order to attach -(CH₃)₂Si-H to the fumed silica surface. This permits the same hydrosilylation reactions to be carried out for A380 as was the case for POSS and avoids excess Si(OH)₂ groups that may lead to electrochemical instability. For both the fumed silica and POSS systems, a neutralization or ion exchange reaction must be carried out in order to make the lithium salts.

Different solvent/temperature treatments were employed to attach the silanes to the fumed silica. The materials were characterized using thermogravimetric analysis (TGA), elemental analysis and atomic absorption spectroscopy. For example, Figure 1 shows a TGA curve for both the silane 2-(4-chlorosulfonylphenyl) ethyl trichlorosilane as well as the silane attached to fumed silica. The silane itself does not completely

decompose at 800°C. Thus in order to quantify the amount of silane attached to the fumed silica using TGA we employed normalized weight losses, and confirmed using elemental analysis that the weight loss from the silane calculated this way corresponded to that obtained by elemental analysis. Nearly optimal amounts of covalently attached chlorosilane were obtained by using toluene as the silanization solvent followed by rinsing with both toluene and methanol and subsequent drying in a vacuum oven at room temperature. It is critical to quantify the amount of attached silane in order to evaluate the lithium concentration expected for complete ion exchange.

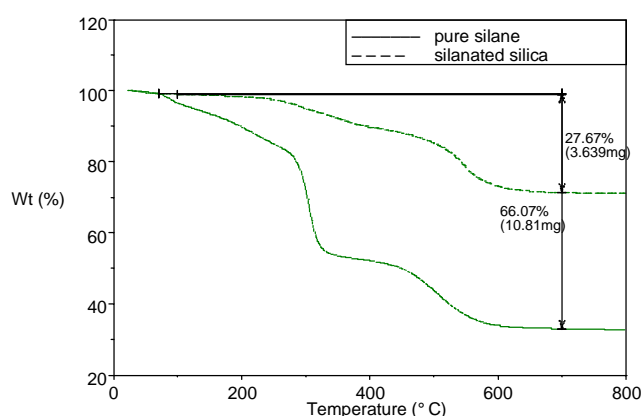


Figure 1. TGA of 2-(4-chlorosulfonylphenyl) ethyl trichlorosilane and silane attached to silica

Several methods of lithium ion exchange were employed, including titration with LiOH and Li acetate in both aqueous and non-aqueous media, and dialysis against Li benzoate in water. Atomic absorption spectroscopy was used to quantify the amount of Li ion.

Films were prepared using the silanated fumed silica and high molecular weight (600,000) polyethylene oxide (PEO). Tough films could be prepared with up to ~30wt% silanated silica by casting from acetonitrile. Preliminary conductivity measurements were made for both the films and for the Li-ion exchanged fumed silica in dimethyl formamide (DMF), and compared with the model compound lithium benzene sulfonate.

