Increasing the Ionic Conductivity of Alkali Carbonphosphonitride Thermosets through Plasticization and Formulation

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Abstract

Alkali dicyanamide ($AN(CN)_2$, A = Li, Na, K, Rb, Cs) reacts with phosphorus cyanide ($P(CN)_3$) in a 2:1 or greater mole ratio in any anhydrous non-protic mutual solvent to form a resin. We will report our systematic efforts to increase alkali ion conductivity by introducing small amounts of non-volatile poly(oxoethylene) based plasticizers, and by copolymerizing the resin with other cyano monomers to increase the alkali concentration. We also mixed highly conductive ceramic powders such as LLZO with the resins to use as binders to prepare a composite. Additionally, combustibility was tested to determine how much plasticizer can be added without compromising the inherent non-flammability of the thermoset materials.

Keywords

Ionic conductor; Lithium; Sodium; Plasticizer; Cyano; Flammability; Thermoset

Introduction

The reaction of phosphorus cyanide $P(CN)_3$ with alkali (Li, Na, K, etc) dicyanamides or other related cyano compounds in any mutual non-protic solvent results in a thermosettable resin which has ionic conductivity, forms adherent films on glass and some metals.[1-2] While still solvated, conductivity of the Li-P-C-N solid at 25 °C can be as high as 10^{-7} S/cm, but on thermal treatment, the C≡N groups polymerize,[1-3] along with other processes, resulting in an amorphous dark red solid. Full cure, to where the solid state NMR is unchanging, requires >2h at 250-275 °C. Once cured, the polymeric material is non-flammable. Such a liquid processable electrolyte could be useful for metal-ion batteries, but the ionic conductivity of the fully cured material at $10^{-13} - 10^{-11}$ S/cm at 300K - far too low to be a practical electrolyte. To improve the conductivity we are exploring plasticization of the cured resin, increasing the alkali ion concentration, variation of the organic solvent used, and using the resin as a binder/filler for more conductive materials [12].

Experimental

The syntheses of $P(CN)_3$ and $LiN(CN)_2$ were described previously. [1-4] Pyridine, tetramethylurea (TMU), and 1,3-dimethyl-2-imidazolidinone (DMIZ) were dried with 3 Å molecular sieves, and acetonitrile (MeCN), 1,2-dimethoxyethane (DME), and sulfolane were vacuum distilled from suitable drying agent (e.g., P_2O_5, Na–benzophenone ketyl) before bringing into an inert atmosphere drybox. Lithium Lanthanum Zirconium Oxide (LLZO) powder was obtained from MSE supplies. Polyethylene glycol dimethyl ether 500 (PEG 500 dimethyl ether), DMIZ, TMU, and $NaN(CN)_2$ were obtained from Sigma-Aldrich and the other solvents from Fisher Scientific. The PEG 500 dimethyl ether was dried by heating the liquid under dynamic vacuum to 200 °C in an oil bath for 16 hours under dynamic vacuum and the resulting anhydrous, light orange oil was kept under argon. All reagents were stored and all reactions were conducted in an argon filled drybox. Samples were cured on a temperature controlled hotplate before being removed for *ex situ* analysis. Reactions between $P(CN)_3$ and $AN(CN)_2$ (A=Li, Na) were conducted in standard 20 mL glass scintillation vials with ~0.1 g $P(CN)_3$ and the appropriate mole ratio of other reactants in 2-4 g of the anhydrous solvent and were allowed to react in the vial for a day before application onto the substrate. Reactions in DME, unlike other solvents, produced a dense, deeply colored secondary liquid phase ('goo') that was separated from the colorless supernatant and redissolved in acetonitrile prior to application. Circles of Pallflex® tissue quartz (from VWR) were punched out and heated at 900 °C under vacuum to remove surface moisture and hydroxyl groups prior to infiltration with liquid resin. LLZO powder was pressed into pellets for infiltration with resin or mixed with resin and cured on a metal coupon.

Complex dielectric permittivity (from 10^6 to 10^{-2} Hz) was measured by dielectric relaxation spectroscopy (DRS) via a Novocontrol Alpha analyzer, under vacuum in a cryostat (Cryo Industries Model 1899-350).

For measurement of conductivity by impedance spectroscopy (EIS) in coin cell configuration, each side of a A-P-C-N electrolyte infiltrated in Pallflex® fiber paper was treated with 10 μL of dry diglyme. The swelled electrolytes were placed between two tin blocking electrodes and sealed within 2032 type coin cells with spacer and wave spring.

The voltage stability windows of Li-P-C-N electrolytes were similarly assessed using asymmetrical coin cells with one tin and one Li metal electrode. With the tin metal electrode taken as the working electrode, linear sweep voltammetry was used to assess the electrochemical stability window. In a typical experiment, the sample was held at 150 °C while the voltage was swept in the positive direction starting from open circuit voltage (OCV) at a scan rate of 10 mV/s until a sharp rise in current was observed. The same experiment was repeated with a fresh electrolyte sample in the negative direction to assess the reductive stability.

Results

The most successful methods of achieving A-P-C-N electrolyte with good top and bottom electrode contacts was found to be: a) depositing films on 0.75 " x 0.75" x .125" thick copper plates with a Sn foil top electrode melted on, and b) repeatedly impregnating silica fiber paper with liquid resin and curing on a hotplate. Efforts to produce composites of our resins and LLZO are still in progress. We know from prior work [1-2] that the reaction between $LiN(CN)_2$ and $P(CN)_3$ consumes 2 eq of the dicyanamide per mole of $P(CN)_3$, any excess dicyanamide remains unreacted, and some of the solvent participates in the likely radical reaction that incorporate it into the product. Furthermore, the excess dicyanamide will trimerize or polymerize at elevated temperatures,[4-9] and these species are undoubtedly present in material cured above 250 °C.

Samples were prepared with excess $LiN(CN)_2$ or LiCN to increase the mobile Li^+ ion concentration and their behavior compared to pressed pellets of $LiN(CN)_2$ that were thermally trimerized/polymerized [4], and data is displayed in Figure 1. Addition of 0.7 eq of LiCN to Li-P-C-N (turquoise right-facing triangles) showed little improvement in conductivity, similar to a sample incorporating double the amount of $LiN(CN)_2$ (pale green left-facing triangles). However, adding a large excess of LiCN (2 eq) produced a dramatic (3 order-of-magnitude) increase in conductivity (blue upright triangles). This material was prepared in pyridine because of the much higher solubility of LiCN in that solvent compared to DMIZ, and these conductivities are only slightly lower than pressed sintered pellets of trimerized/polymerized $LiN(CN)_2$ (black squares and red circles). Sodium dicyanamide is quite soluble in DMIZ, and Na-P-C-N materials were prepared in this solvent both with and without addition of PEG-500 plasticizer. Even without added plasticizer, the Na-P-C-N materials are about 2 orders of magnitude more conductive (orange diamonds) than the equivalent Li variety, and the addition of about 35 wt % plasticizer increased the conductivity nearly 100-fold (periwinkle down-facing triangles). Samples of Li-P-C-N containing PEG-500 (brown points) had only negligible

improvements in conductivity. In most cases the activation energies are about 35 J/mol-K, but the upward curve in the lines for the pellets shows an unusual non-linear dependence of E_a on temperature.
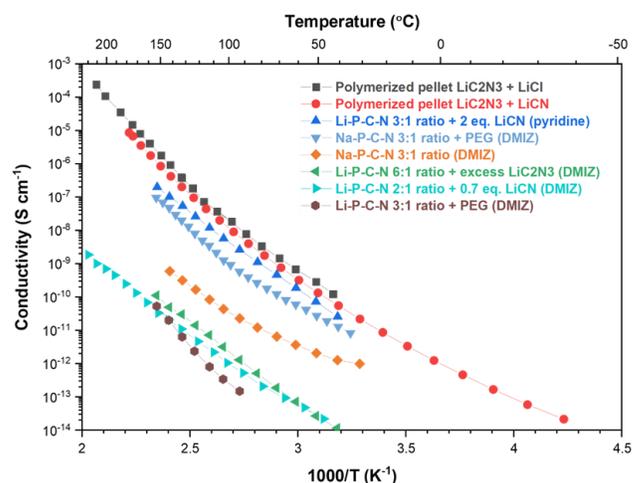

Figure 1. DRS conductivity data on cured A-P-C-N materials impregnated in silica fiber paper. Black squares and red circles show data typical for a pressed pellet (without fiber paper support) of polymerized LiC_2N_3 containing other Li salts: 36 mol% LiCN (red circles) or 34 mol% LiCl (black squares), respectively.

Electrochemical impedance spectroscopy (EIS) was conducted to assess the impact of diglyme plasticization on ionic conductivity. For two different electrolyte formulations shown above, the 6:1 $LiN(CN)_2$:$P(CN)_3$ material (blue upright triangles) and 3:1 $LiN(CN)_2$:$P(CN)_3$ + 2 eq LiCN (pale green left-facing triangles), the room temperature ionic conductivities with added diglyme plasticizer increased to 1 x 10^{-7} S/cm, and 6 x 10^{-8} S/cm respectively. The large conductivity improvement likely stems from the ability of the plasticizer to facilitate ion dissociation (leading to more charge carriers) and assist in vehicular ion transport (leading to enhanced ion mobility).

Solid state ^{13}C (MAS) NMR spectra show that the carbon-containing moieties in Na-P-C-N materials are similar regardless of whether PEG plasticizer is included in the reaction. Peaks ascribed to the Na-P-C-N backbone show up around +120 ppm (cyano species) and +165 ppm (triazine/heptazine moieties). A peak at +71 ppm corresponds to the PEG backbone carbons. The two peaks at +33 ppm and +48 ppm, arise from either residual DMIZ (methyl groups) trapped in the thermoset of from reaction of the starting materials with DMIZ, incorporating it into the final product.

In order to assess the voltage stability of the Li-P-C-N materials linear sweep voltammetry was used to assess the

electrochemical stability window for the formulations. The 6:1 LiN(CN)2:P(CN)$_3$ material is quite stable over a window of -2 V to about 5 V vs Li/Li$^+$, while the 3:1 LiN(CN)$_2$:P(CN)$_3$ + 2 eq LiCN sample has a fairly quick onset of degradation current exceeding 1 μA below -1 V and above 3 V vs Li/Li$^+$. The lower voltage stability window of the 3:1 LiN(CN)$_2$:P(CN)$_3$ + 2 eq LiCN sample may be attributed to the excess LiCN, indicating the addition of LiCN may pose a potential tradeoff between enhanced conductivity (in the dry state) and decreased voltage window. LiBF$_3$CN was reported to have some degradation under reductive conditions [11].

Discussion

It is clear from the results that both increasing the alkali ion concentration and adding organic plasticizers have a positive effect on the ionic conductivity, but the level of improvement is still insufficient. While addition of diglyme has a dramatic effect, that is probably from the coordination of Li$^+$ ions with a small molecule, and that is not compatible with the goal of a non-flammable solid electrolyte. The higher conductivity for the Na-P-C-N system is intriguing, and justifies an examination of the entire alkali series, which is presently underway. Ceramic materials with high alkali ion conductivities are known [10], but are not solvent processable. Efforts to prepare composites of A-P-C-N resins and LLZO are still in progress.

Acknowledgements

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