Nanocomposite Electrolytes Using Single-Ion Conducting Fumed Silica

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Rechargeable lithium batteries are potential candidates for safe and reliable electrochemical power sources with high-energy density and long-cycle life. Lithium metal anodes would provide high energy density, but reaction with liquid electrolyte forms a passivation layer that produces poor material utilization. Additionally, formation of lithium dendrites during charge leads to safety concerns. To overcome these problems, work has generally focused on development of novel electrolytes with both high conductivity and limited reactivity with lithium metal anodes. Electrolytes based on high-molecular weight dielectric polymer hosts, most commonly polyethylene oxide (PEO), inhibit dendrite formation during charge and are less reactive with lithium than liquid electrolytes. However, room-temperature conductivities of PEO-based polymer electrolytes are low (10^{-6} to 10^{-3} S cm^{-1}) due to limited ion mobility in the largely crystalline phase and the coupling of ion motion with polymer chain segmental motion. A high room-temperature conductivity (10^{-3} S cm^{-1}) can be obtained by adding polar liquid solvents to disrupt polymer crystallization and decouple ion movement from polymer chain motion. However, the improved conductivity is based on the mobility of both cations and anions. The migration of anions results in a polarization potential, which consequently decreases ionic transport. This problem has spurred attempts to design single-ion conducting polymer electrolytes where anionic moieties are covalently anchored to the polymer chains. Unfortunately, these attempts, despite ingenuity, have met with limited success either in terms of conductivity or electrochemical stability.

Our laboratory has been exploring composite electrolytes for lithium batteries that consist of dispersions in a liquid electrolyte of nanometer-size fumed silica with tailored surface characteristics. The fumed silica additive forms a continuous layer that produces poor material utilization. Additionally, formation and long-cycle life. Lithium metal anodes would provide high energy density, and reliable electrochemical power sources with high-energy density.

Fumed silica surfaces were chemically modified to form single-ion conductors by attaching lithium-exchanged anionic groups (lithium 2-acrylamido-2-methyl-1-propanesulfonate, LiAMPS) to surface methacrylates on Degussa R711 fumed silica (abbreviated as R711-pLiAMPS). Surface lithium contents varying from 0.7 to 9.1 nm^{-2} were synthesized. Conductivity and transference number measurements were conducted on nanocomposite electrolytes containing polyethylene glycol dimethyl ether (PEGdm) + R711-pLiAMPS. A maximum room-temperature conductivity of 4.5 \times 10^{-6} S cm^{-1} was obtained at a surface Li\(^{+}\) content of 4.2 nm^{-2} and a Li:O mole ratio of 1:100 (15.8 wt % filler) with a Li\(^{+}\) transference number of 0.59. A maximum Li\(^{+}\) transference number of 0.78 was achieved at a surface Li\(^{+}\) surface content of 4.2 nm^{-2} and a Li:O mole ratio of 1:20 (48.5 wt % filler) with a conductivity of 2.2 \times 10^{-6} S cm^{-1}. Adding lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) to the samples enhances room-temperature conductivity by more than two orders of magnitude while still maintaining a relatively high Li\(^{+}\) transference number.

High-transference number nanocomposite electrolytes were prepared by dispersing R711-pLiAMPS into oligomeric polyethylene glycol dimethyl ether (PEGdm), where lithium imide salt may be added to assist ionic transport. Room-temperature conductivity and Li\(^{+}\) transference number (t_{Li\(^{+}\)}) are reported of these composite electrolytes.

Experimental

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Electrolyte preparation.—Polyethylene glycol dimethyl ether (PEGdm, Mw 250, Aldrich) was dried over 4 Å molecular sieves for at least one week. The reagent 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS, Aldrich) was dried in a vacuum oven at 40°C for 1 week. Lithium bis(trifluoromethylsulfonyl)imide (LiN(CF\(_3\))\(_2\))\(_3\), LiTFSI, 3M) and fumed silica containing methacrylate surface group (R711, Degussa) were dried in a vacuum oven at 100°C for at least 3 days before use. Lithium hydroxide (LiOH, Aldrich) and 2,2’-azoisobutyronitrile (AIBN, Aldrich) were used as received.

R711-poly(2-acrylamido-2-methyl-1-propanesulfonate) (R711-pAMPS) was prepared by stirring R711 with AMPS in N,N-dimethylformamide (DMF) at 65-70°C overnight in a refluxed reactor, using AIBN as the radical initiator. Various weight ratios of R711:AMPS ranging from 1.06 to 19.4 were used with 10 g L^{-1} of R711 to produce a series of R711-PAMS with differing surface coverage. The AIBN content used was 0.5 wt % based on total weight of R711 + AMPS. After completion of the reaction, the mixture was transferred to a beaker and placed in a fume hood for 5 days to vaporize DMF, followed by drying in a vacuum oven at 90°C for 3
days. The as-prepared R711-pAMPS powders were washed with deionized water three times to remove the unattached polyelectrolyte poly(2-acrylamido-2-methyl-1-propanesulfonic acid) and unreacted AMPS. The washed R711-pAMPS was dried in a vacuum oven at 90°C for 3 days. The dry-weight ratio of washed R711-pAMPS to unwashed R711-pAMPS is \( w / W \).

LiOH was added to R711-pAMPS dispersed in water to exchange hydrogen to lithium ion. The resulting R711-pLiAMPS powder was washed with methanol to remove the excess LiOH and then dried under vacuum at 100°C for at least 3 days. The surface number density of Li\(^+\) (\( \gamma \), number of Li\(^+\) per \( \text{nm}^2 \)) of the R711-pLiAMPS was calculated by

\[
\gamma = \frac{\text{Li}^+ \text{ number}}{\text{silica surface area}}
\]

\[
= \frac{(\text{R711 weight} + \text{AMPS weight})(w/w) - \text{R711 weight}}{\text{AMPS molar weight}}
\]

\[
= \frac{N_A}{\text{R711 weight}(\text{R711 specific surface area})}
\]

where \( N_A \) is Avogadro’s number, and the R711 specific surface area is 150 \( \text{m}^2 \text{ g}^{-1} \). Three samples were measured for every ratio of R711:AMPS, giving an uncertainty in \( \gamma \) of \( \pm 20\% \).


\textbf{Figure 1.} Room-temperature infrared spectra of R711, LiAMPS, and R711-pLiAMPS (\( \gamma = 4.2 \text{ nm}^{-2} \)).

\textbf{Figure 2.} Conductivity of R711-pLiAMPS + PEGdm composite electrolytes (Li:O = 1:100); (a) temperature dependence of conductivity, (b) room-temperature conductivity as a function of Li\(^+\) surface concentration \( \gamma \).

\textbf{Results and Discussion}

\textit{FTIR of R711-pLiAMPS.}—Figure 1 shows the FTIR spectra of R711, LiAMPS, and R711-pLiAMPS (\( \gamma = 4.2 \text{ nm}^{-2} \)) at room temperature. The IR spectrum of R711-pLiAMPS shows not only the characteristic adsorption bands of R711 (Si-Si at 1100 cm\(^{-1}\), Si-O-Si at 1210 cm\(^{-1}\), and C=O at 1720 cm\(^{-1}\)) but also the characteristic bands of LiAMPS (N-H at 1550, C=O at 1666, and CH\(_2\) at 2850-3000 cm\(^{-1}\)). These results confirm that LiAMPS has been successfully anchored onto the surface of R711.

\textit{Effect of surface Li\(^+\) content.}—With the dissociable Li\(^+\) sulfonate group on the surface, R711-pLiAMPS has the characteristics of a single-ion conductor with conductivity dependent on the Li\(^+\) surface concentration \( \gamma \). Figure 2a shows the temperature dependence of the conductivity of R711-pLiAMPS + PEGdm composite electrolytes at a constant Li:O mole ratio of 1:100. We find \( \gamma \) affects ionic conductivity across the entire temperature range. The effect of Li\(^+\) surface concentration on the room-temperature conductivity is illustrated in Fig. 2b. As the surface density of Li\(^+\) increases, the wt \% of R711-pLiAMPS in the matrix decreases (upper abscissa in Fig. 2b) and the room-temperature conductivity passes through a maximum. At low Li\(^+\) surface density, the low conductivity is due to the high-particle loading, which results in an overly tortuous path for lithium ions to travel through the network. However, the low conductivity at high Li\(^+\) surface density is caused by large inter-particle
distance of R711-pLiAMPS filler, which is a result of low-particle loading. As a result, a maximum room-temperature conductivity of $4.5 \times 10^{-6}$ S cm$^{-1}$ is achieved at $\gamma = 4.2$ nm$^{-2}$.

Effect of Li:O mole ratio.—Figure 3 shows the effect of Li:O mole ratio on the ionic conductivity of R711-pLiAMPS ($\gamma = 4.2$ nm$^{-2}$) + PEGdm composite electrolytes. Below a Li:O mole ratio of less than 1:100, the room-temperature conductivity increases with increase in Li:O mole ratio because more lithium ions are added to the system. However, the conductivity dramatically decreases after the Li:O mole ratio exceeds 1:100. The decrease of conductivity may be ascribed to the formation of an overly tortuous path for the lithium ions to travel because an integrated three-dimensional network is formed at these high-particle loadings.

The Li$^+$ transference numbers of R711-pLiAMPS ($\gamma = 4.2$ nm$^{-2}$) + PEGdm composite electrolytes were measured to be 0.59 and 0.78 at a Li:O mole ratio of 1:100 and 1:20, respectively. A transference number of unity is expected for these electrolytes because the anionic moieties are covalently anchored to silica surface. Therefore, the transference number of less than unity indicates that one or more other mobile ionic species are present in the electrolyte, which are presumably reaction products of solvent and lithium. However, compared with those (0.2-0.4) of conventional polymer electrolytes, these $t_{\text{Li}^+}$ values are high.

Effect of LiTFSI salt content.—Although an optimized conductivity ($4.5 \times 10^{-6}$ S cm$^{-1}$ at $\gamma = 4.2$ nm$^{-2}$ and Li:O = 1:100) for R711-pLiAMPS + PEGdm composite electrolytes was achieved, this value is too low for practical battery applications. LiTFSI salt was hence added to provide additional (and more mobile) charge carriers. Figure 4 shows the room-temperature conductivity and Li$^+$ transference number of R711-pLiAMPS ($\gamma = 4.2$ nm$^{-2}$) + LiTFSI + PEGdm composite electrolytes as a function of LiTFSI content. Both R711-pLiAMPS and LiTFSI contents vary such that (a) Li(total):O = 1:20 and (b) Li(total):O = 1:100. At 100% LiTFSI, the electrolyte is liquid because no fumed silica is present.

Figure 3. Effect of Li:O mole ratio on the conductivity of R711-pLiAMPS ($\gamma = 4.2$ nm$^{-2}$) + PEGdm composite electrolytes; (a) temperature dependence, (b) room-temperature conductivity. Inset table on (b) reports lithium transference number for two compositions.

Figure 4. Room-temperature conductivity and Li$^+$ transference number of R711-pLiAMPS ($\gamma = 4.2$ nm$^{-2}$) + LiTFSI + PEGdm composite electrolytes as a function of LiTFSI content. Both R711-pLiAMPS and LiTFSI contents vary such that (a) Li(total):O = 1:20 and (b) Li(total):O = 1:100. At 100% LiTFSI, the electrolyte is liquid because no fumed silica is present.
Conclusion

Single-ion conductors R711-pLiAMPS were successfully synthesized using a radical reaction followed by ion exchange. Both the room-temperature conductivity and Li\(^+\) transference number of R711-pLiAMPS + PEGdm composite electrolytes were adjusted by varying Li\(^+\) surface concentration and Li:O mole ratio. The highest conductivity obtained is 4.5 \times 10^{-6} \text{ S cm}^{-1} at a Li\(^+\) surface concentration of 0.42 nm\(^2\) and a Li:O mole ratio of 1:100, and the largest Li\(^+\) transference number is 0.78 at a Li\(^+\) surface concentration of 4.2 nm\(^2\) and a Li:O mole ratio of 1:20.

Composite electrolytes consisting of R711-pLiAMPS + LiTFSI + PEGdm were also prepared and studied. The addition of LiTFSI improves the room-temperature conductivity by more than two orders of magnitude while keeping a relatively high Li\(^+\) transference number of 0.5.

Acknowledgments

We gratefully acknowledge funding from the Department of Energy, Office of Basic Energy Sciences and Office of Freedom-CAR and Vehicle Technologies.

North Carolina State University assisted in meeting the publication costs of this article.

References


