Ionic Conductivity of New Ambient Temperature Alkali Metal Glasses $AlCl_3/NaN(CN)_2$

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Ambient temperature alkali glassy salt mixtures, $x[AlCl_3]/(1 - x)[NaN(CN)_2]$ ($x = 0.4-0.75$), were prepared. A large increase in the C≡N stretching frequencies for these materials indicate complex formation between the anion $[N(CN)_2]^-$ and $AlCl_3$ molecule. Ab initio calculations confirm the assignments of the vibrational frequencies. The 1:1 adduct has a glass transition at 27 °C, and the glassy state persists for 4 weeks at room temperature. The room temperature ionic conductivity of this glass is 6.6×10^{-6} S/cm, and it increases as the $AlCl_3$ content increases. The temperature dependence of the conductivity follows the Vogel−Tamman−Fulcher equation, suggesting that ion transport is coupled to local motion in the glassy salt mixture system.

Introduction

Ambient temperature glasses are potentially useful electrolytes for high-energy batteries.[1−4] These materials are prepared by the complex of salts and a Lewis acid, such as $AlCl_3$. Complex formation between the Lewis acids and the anion should delocalize the negative charge and thereby decrease the Coulombic attractions between cations and anions. The coordination of $AlCl_3$ with the anion of a salt results in either ionic liquids or crystalline materials, which exhibit low melting points. Salts containing alkylammonium cations, such as butylpyridinium chloride and 1,3-dialkylimidazolium chloride, interact with $AlCl_3$ to form ionically conducting liquids at room temperature.[2−4] Other complicated organic halide salts including triazolium,[5] tetraalkylammonium, and trialkylsulfonium[6] cations form ionic liquid systems via the complexation of $AlCl_3$. The formation of ionic liquids rather than crystalline solids may be attributed to the irregular shapes of the organic cations, which frustrate crystallization. Similarly, trifluoromethyl sulfonate[1] and bis(trifluosulfonyl)imide[7] (TFSI), salts containing 1,3-dialkylimidazolium or tetraalkylammonium[8] cations, produce room temperature organic ionic liquids without the complexation of $AlCl_3$. These observations suggest that ion packing may be manipulated to form ionic liquids.

By contrast, the alkali metal salt/$AlCl_3$ adducts generally are crystalline material with low melting points.[9] For instance, the NaCl−KCl−$AlCl_3$ molten salt system exhibits a melting point as low as 70 °C.[10] However, the large concentrations of $AlCl_3$ needed to optimize the conductivity result in fairly high vapor pressures, which are undesirable when a battery is operated at high temperatures. To obtain ambient temperature alkali metal glassy salts, the choice of alkali metal salts is crucial, and only a few ambient temperature alkali metal glassy salt systems possess chemical properties that fulfill the requirements for battery electrolytes.[11−14] For example,[11] Xu showed that the $LiN(SO_2Cl)(SO_2F)$ salt, which has a glass transition temperature of 25 °C, reacts with $AlCl_3$ to form a 1:1 adduct with a glass transition temperature of −35 °C and ionic conductivity around 4×10^{-6} S/cm at room temperature.[11] Similarly, Liu et al.[12,13] showed that the 1:1 LiSCN/$AlCl_3$ adduct can be supercooled to produce a material with a glass transition temperature of −15 °C and ionic conductivity around 4×10^{-4} S/cm at room temperature. The glassy properties of this 1:1 LiSCN/$AlCl_3$ adduct may originate from the ambidentate character of the thiocyanate anion, which may coordinate to $AlCl_3$ molecules through either S or N, and thereby bridge other $AlCl_3$ molecules, to produce a complicated network that resists crystallization.

In the present research, we consider another alkali pseudohalide salt, $NaN(CN)_2$, as a candidate for glass

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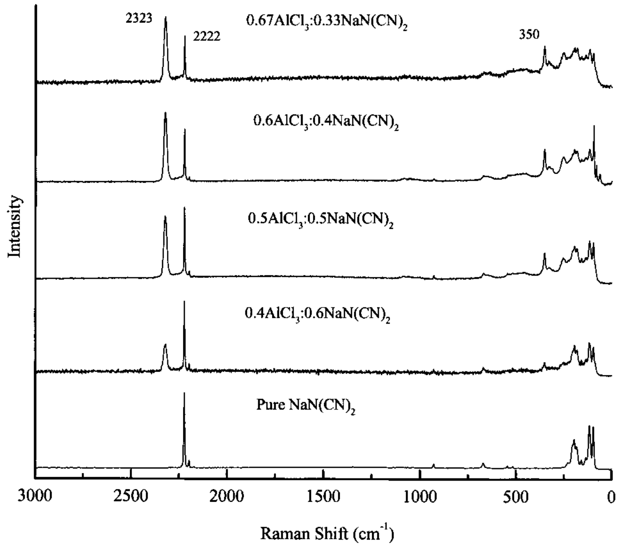


Figure 1. Raman spectra of $AlCl_3/NaN(CN)_2$ mixtures.

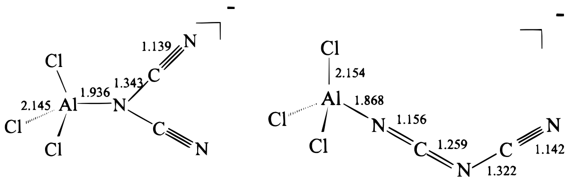
formation in the presence of $AlCl_3$. The $N(CN)_2^-$ anion has three resonance forms, and the negative charges may delocalize over the imide nitrogen atom, as well as the two cyano nitrogen atoms, each of which may coordinate to $AlCl_3$. The 1:1 adduct $NaN(CN)_2{\cdot}AlCl_3$ can be supercooled, and the resulting material exhibits a glass transition temperature of 27 °C. The ionic conductivity of this glass is around 6×10^{-6} S/cm at room temperature, and the glassy state persists for at least 4 weeks at room temperature under an inert atmosphere.

Experimental Section

Aluminum chloride (99.99%) and sodium dicyanoimide (96%) were purchased from Aldrich Chemical Co. Sodium dicyanoimide was dried under high vacuum ($<5 \times 10^{-5}$ Torr) at 150 °C for 3 days and then stored and handled in a dry nitrogen-filled glovebox. Aluminum chloride was sublimed three times following the procedure described in the literature.[15] The compounds were pulverized in a mortar and mixed in specific ratios. These mixtures were transferred into sample vials and melted at 150 °C under a dry nitrogen atmosphere. Tiny magnetic stir bars were used to produce homogeneous mixtures. The vial was then removed from oil bath and allowed to cool to room temperature. These naturally cooled samples were used in determinination of ionic conductivities and Raman spectra. The conductivity cell was loaded in the drybox, and ionic conductivity measurements were performed between 10 and 75 °C with a HP 1286 impedance analyzer over the frequency range from 13 MHz to 5 Hz. Temperature control was achieved with a Sun system environmental chamber. Samples for DSC measurements were loaded in hermetically sealed pans, and data were obtained with a Perkin-Elmer Pyris DSC 1. Raman spectra were obtained with a Biorad FT spectrometer on samples and sealed in capillary tubes. These amorphous samples display weak and broad bands in contrast with more distinct bands of crystalline samples. The spectral resolution of the interferometer was 4 cm^{-1}.

Results and Discussions

Raman Spectra. The Raman specta of pure $NaN(CN)_2$ and a series of $AlCl_3/NaN(CN)_2$ adducts are illustrated in Figure 1. Solid $NaN(CN)_2$ has two strong features in the C≡N stretch frequency region of the Raman spectrum; a major peak at 2222 cm^{-1} is assigned to the symmetric C≡N stretch of the $N(CN)_2$ anion, and a less intense peak at 2198 cm^{-1} is assigned to the asymmetric stretch.[16] Crystalline $AlCl_3$ has a sharp peak in the Raman spectrum at 309 cm^{-1}, assigned as the symmetric stretching mode (ν_2^- A_{1g}), by comparison with published results.[17,18] The Raman spectrum of the $NaN(CN)_2{\cdot}AlCl_3$ exhibits a broad vibrational band at 2323 cm^{-1}, which represents an increase of 100 cm^{-1} relative to the C≡N stretch of $NaN(CN)_2$. This frequency increase indicates the formation of a link between the nitrogen atom of the CN group in the dicyanoimide anion with the $AlCl_3$ molecule.[12,17,19] The increase in the breadth of the C≡N band upon complex formation is attributed to the existence of a variety of local site geometries of the aluminum trichloride dicyanoimide complex in the glassy salt mixture. A peak at 2222 cm^{-1} in the 1:1 mixture is assigned as either the C≡N stretching mode for structure **2b**, Figure 2, or, more likely, the presence of some uncomplexed dicyanoimide salt. Electronic structure calculations described in the next section indicate that a peak at 350 cm^{-1} is the $AlCl_3$ symmetric stretching mode of $[AlCl_3N(CN)_2^-]$. However, the $AlCl_4^-$ anion also has a breathing mode at 351 cm^{-1}, and the existence of $AlCl_4^-$ in this salt mixture cannot be ruled out. Raman spectra for $AlCl_3/NaN(CN)_2$ mixtures with different stoichiometric ratios are shown in Figure 1. As the $AlCl_3$ content increases, the intensity of the peak at 2323 cm^{-1} increases, and that at 2222 cm^{-1} decreases. For the $AlCl_3/NaN(CN)_2 = 2{:}1$ a feature at 308 cm^{-1} indicates the presence of $AlCl_3$ in this $AlCl_3$-rich mixture.



2a **2b**

Figure 2. Two proposed structures for the $AlCl_3N(CN)_2^-$ anion.

Ab Initio Calculation. The electronic structures of the $N(CN)_2^-$ and $AlCl_3N(CN)_2^-$ anions were determined by ab initio molecular orbital calculations[19] at the Hartree–Fock level with the split-valence plus polarization 6-31G* basis set. The binding energy for sodium dicyanoimide in the gas phase is defined by the following reaction:

$$NaN(CN)_{2(g)} \rightarrow Na^+_{(g)} + N(CN)_2{}^-{}_{(g)} \quad \Delta E$$

At the HF/6-31G* level, the sodium affinity of $NaN(CN)_2$

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was determined to be 110 kcal/mol, which is slightly lower than that of NaSCN (118 kcal/mol). Two different structures of the complex $AlCl_3N(CN)_2^-$ were explored in which either the imide nitrogen atom (**2a**) or the cyano nitrogen atom (**2b**) coordinates to the aluminum center, as illustrated in Figure 2. For the isolated $N(CN)_2^-$ ion, at the HF/6-31G* level of theory, the imide nitrogen atom has a more negative Mulliken charge than the cyano nitrogen. This suggests that the imide nitrogen atom might be the site of coordination by $AlCl_3$. However, calculations at the HF/6-31 G* level indicate that structure **2b** is more stable than **2a** by 8 kcal/mol; this energy difference may result either from steric hindrance between the aluminum center and the $N(CN)_2^-$ moiety in **2a** or from charge reorganization following complex formations. The structures of **2a** and **2b** were calculated for the gas-phase species ($\epsilon = 1$), but the energy difference between these two isomers is expected to be smaller in the real system because of the influence of the surrounding dielectric medium.

At the HF/6-31G* level (scaled by a factor of 0.91), structure **2a** is calculated to possess two Raman-active modes at 2311 and 2338 cm^{-1} in the C≡N stretching region. These values fall on either side of the broad peak observed at 2323 cm^{-1} in the observed Raman spectrum. For structure **2b**, two modes are calculated at 2320 and 2237 cm^{-1} in the C≡N stretching region, consistent with experimental observations. In the low wavenumber region, a vibrational transition at 358 cm^{-1} is calculated for the $AlCl_3$ symmetric stretch of **2a**, and a 350 cm^{-1} absorption is calculated for the breathing mode for structure **2b**. These ab initio calculations are in reasonable agreement with experimental data, 2323 and 2222 cm^{-1}, and indicate that **2a** and **2b** are reasonable species in the $AlCl_3/NaN(CN)_2$ mixture. The Al−Cl stretching frequencies in the Raman spectra for the two isomers of $AlCl_3N(CN)_2^-$ anion are similar to those of $AlCl_4^-$.

DSC Measurement. Solid $NaN(CN)_2$ decomposes at 410 °C, and no melting point is observed. When the $x[AlCl_3]/(1-x)[NaN(CN)_2]$ ($x > 0.4$) mixtures are melted at 150 °C and naturally cooled to room temperature, a glass is formed that persists for at least 4 weeks at room temperature under an inert atmosphere. Figure 3a shows the DSC scan traces upon heating of the naturally cooled and quenched 1:1 adduct. The naturally cooled 1:1 adduct has a glass transition temperature around 27 °C and several small endothermic peaks between 85 and 100 °C. When the sample is quenched with a cooling rate faster than 460 °C/min, these peaks disappear, and a single glass transition is observed at ca. 31 °C. The DSC data for the supercooled mixtures with different stoichiometric ratios are shown in Figure 3b where it may be seen that the glass transition temperatures decrease as the $AlCl_3$ content increases, and this decrease is accentuated as the $AlCl_3$ molar ratio increases from 0.6 to 0.7. The glass transition temperatures for quenched samples are higher than those obtained on slowly cooled samples. After 4 weeks, the glassy state persists, but DSC data reveal an endotherm at 86 °C, which indicates partial crystallization.

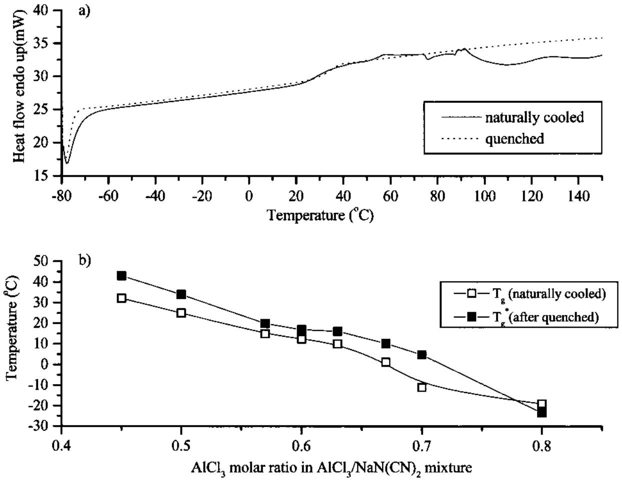

Figure 3. Thermal analysis of the $AlCl_3/NaN(CN)_2$ mixtures. (a) The DSC traces of 1:1 adduct. The full line denotes the upscan of naturally cooled sample, and the dotted line denotes the upscan of quenched sample. (b) Glass transition temperatures T_g (naturally cooled in air) and T_g* (quenched) of the $AlCl_3/NaN(CN)_2$ mixtures.

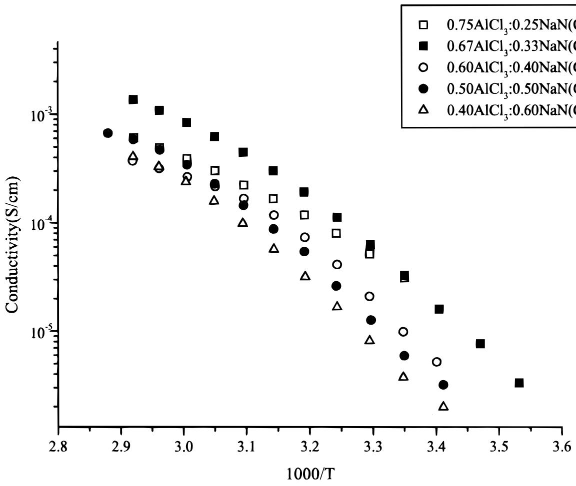

Figure 4. Ionic conductivity of $AlCl_3/NaN(CN)_2$ mixtures.

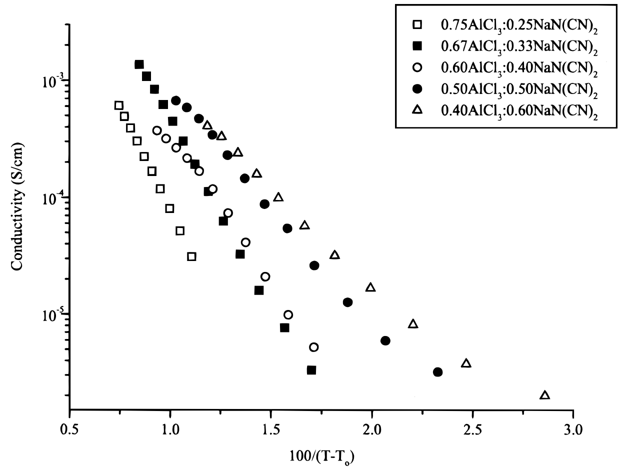

Figure 5. Ionic conductivity versus $100/(T - T_0)$ for $AlCl_3/NaN(CN)_2$ mixtures ($T_0 \approx T_g - 50$).

Ionic Conductivity. Ionic conductivities of $AlCl_3/NaN(CN)_2$ mixtures are shown in Figure 4. For the 1:1 mixture, the ionic conductivity is 7×10^{-4} S/cm at 75 °C and 6×10^{-6} S/cm at 25 °C, and the ionic conductivity increases as the $AlCl_3$ content increases, which correlates with a decrease in the glass transition temperature of the mixtures. The room temperature ionic conductivity reaches a maximum at 2×10^{-5} S/cm for $AlCl_3/NaN(CN)_2$ with the molar ratio of 0.67. The curvature of the conductivity plot reflects the amorphous nature of this salt mixture. The log of the ionic conductivity is plotted versus the $(T - T_0)$ where T_0 represents an empirical parameter related to the glass transition temperature and is usually lower than T_g by 50 K. As shown in Figure 5, the resulting plots are nearly straight, indicating that these salt systems follow the dynamics of amorphous materials. Accordingly, the conductivity plots fit the Vogel–Tamman–Fulcher (VTF) equation:[21]

$$\sigma = AT^{-1/2}\exp(-B/(T - T_0))$$

In this equation, B is a pseudoactivation energy term relating to the expansivity of the host required for ion migration. A stands for the preexponential factor, which is dependent on the concentration of charge carriers. According to the fitted data in Table 1, the A term increases as the $AlCl_3$ content increases, up to a mole fraction of 0.67, and then decreases. Compared with those in the polymer electrolyte $NaCF_3SO_3$/aPEO systems,[22] the B terms for the $AlCl_3/NaN(CN)_2$ systems are generally smaller than that of the PEO system, indicating lower pseudoactivation energies for the ionic inorganic system.

Table 1. VTF Parameters for $AlCl_3/NaN(CN)_2$ System

complex	T_0, K	B, K	A, S $K^{1/2}$ cm^{-1}
$0.4AlCl_3/0.6NaN(CN)_2$	255	429.2	0.11
$0.5AlCl_3/0.5NaN(CN)_2$	250	475.6	0.204
$0.67AlCl_3/0.33NaN(CN)_2$	245	556.8	0.593
$0.75AlCl_3/0.25NaN(CN)_2$	208	800.4	0.46

Both the relatively low value of the conductivity and the bent curves in Figure 4 suggest the coupling of diffusion with the medium, which is in contrast to that in superionic glasses (such as AgCl/AgI/CsCl).[23] The remnant viscosity/transport coupling may arise from the same anionic asymmetry that causes the materials to form a glass.

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