Lithium nitrate and lithium trifluoromethanesulfonate ammoniates for electrolytes in lithium batteries*

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Abstract

The liquid ammonia solutions of lithium nitrate and lithium trifluoromethanesulfonate (triflate) have been found to be highly conductive inorganic electrolytes with low vapor pressures. The important phases of the $LiNO_3 \cdot xNH_3$ solutions ($1.5 < x < 3.1$) and those of the $LiSO_3CF_3 \cdot yNH_3$ solutions ($1.5 < y < 3.5$) are documented. In addition, the temperature dependence of their conductivities, their electrical stability windows, and their NH_3 vapor pressures were determined. In summary, the lithium triflate ammoniate ($LiCF_3SO_3 \cdot 2NH_3$) remains a liquid down to -10 °C. It has an electroactivity range of 3.8 V and a conductivity of 0.6×10^{-3} Ω^{-1} cm^{-1} at -10 °C. The NH_3 vapor pressure is less than 1 bar at 60 °C. The lithium nitrate ammoniate ($LiNO_3 \cdot 2NH_3$) has an electroactivity range of 3.5 V and a conductivity of 2.5×10^{-2} Ω^{-1} cm^{-1} at 20 °C. The freezing point of the nitrate ammoniate is between 3 °C and -10 °C depending on the stoichiometry. Its NH_3 vapor pressure remains below 1 bar up to 40 °C. In addition, Li/MnO_2 batteries were constructed and tested using the above mentioned electrolytes.

Introduction

Ammonia is a convenient solvent for preparing electrolytes suitable for electrochemical generators. The liquid ammonia solutions, also called ammoniates, are potentially useful as electrolytes for batteries [1]. The ammoniates are prepared during the absorption of anhydrous, gaseous ammonia by anhydrous salts such as lithium perchlorate or sodium iodide [1, 2]. Some of their beneficial physical and electrical characteristics include a wide electroactivity range (greater than 3 V), high conductivity (about 10^{-2} Ω^{-1} cm^{-1}), and low NH_3 vapor pressure at room temperature. Ammoniates also have the advantage of remaining inert with regard to alkaline metals.

In this paper we examine the ammoniates of lithium nitrate and lithium triflate.

Experimental

The ammoniates were prepared using anhydrous ammonia (electronic N 45 AIR LIQUIDE) and either lithium nitrate (Aldrich 99.99% Suprapur) or lithium triflate (Aldrich 97%, further dehydrated at 120 °C under vacuum). The synthesis has been described previously [2]. The water content in the ammoniate products was determined to be less than 50 ppm as determined by the Karl Fischer technique.

All experimentation was carried out in a dry box under an argon atmosphere.

The conductivity of the liquid ammoniates was determined by a.c. measurements using a Solartron Model 1170 Frequency Response Analyser.

The ammonia vapor pressure was measured with a calibrated 'CMAC' (SEDEME) gauge. The electroactivity range was determined from voltammograms collected with a Tacussel PRT-20 (potentiostat). A three electrode cell was used where the working electrode was a platinum disk (source of voltage); the counter electrode was lithium metal rod (source of voltage) that also played the role of an Li/Li^+ reference electrode. The scan rate for the voltammograms was 10 mV s^{-1}.

Results and discussion

(i) Physical properties of the ammoniates
    (a) $LiNO_3 \cdot xNH_3$

For ammonia stoichiometries below 1.6, a slurry containing both the liquid ammoniate and the solid lithium nitrate was observed. Liquid ammoniates were obtained for values of x between 1.6 and 3.1. Above 3.1, saturation occurs and no further ammonia is absorbed under 1 bar. Similar behavior was also reported for the lithium perchlorate ammoniate [2]. The freezing point of the liquid lithium nitrate ammoniate varied from 3 °C for $x = 1.6$, to -10 °C for $x = 3.1$.

    (b) $LiSO_3CF_3 \cdot yNH_3$

For ammonia stoichiometries up to 1.5, the lithium triflate ammoniate remains a solid. The solid triflate ammoniate readily adsorbs further NH_3 molecules. For values of y between 1.5 and 3, the ammoniate is a liquid possessing a high viscosity (40 cP at 20 °C) and a density varying from 1.40 g cm^{-3} ($y = 1.7$) to 1.44 g cm^{-3} ($y = 2.3$). The freezing point of the liquid ammoniate appears to be independent of composition and it remains in the liquid state for temperatures down to -15 °C.

When the ammonia content rises above 3, the lithium triflate ammoniate assumes a gel-like consistency. The 'melting' temperature of the gel increases with the ammonia content (i.e., 50 °C for $LiSO_3CF_3 \cdot 3.5NH_3$).

While the study of the various ammoniates is of interest, the present work focuses on ammoniates which remain liquid at room temperature. To this end $LiSO_3CF_3 \cdot 2NH_3$ and $LiNO_3 \cdot 2NH_3$ were studied.

(ii) Vapor pressure studies

The ammonia vapor pressure of the ammoniate liquids was significantly lower than that of concentrated aqueous ammonia. The relationships between the equilibrium NH_3 vapor pressure and the temperature for $LiSO_3CF_3 \cdot 2NH_3$ and $LiNO_3 \cdot 2NH_3$ are presented in Fig. 1. The low vapor pressure (less than 1 bar) of the liquid ammoniates at room temperature is an important safety advantage over electrolytes which must be kept under high pressures under similar conditions. No hysteresis was observed in the vapor pressure–temperature curves for the range of temperatures studied.

(iii) Conductivity

The conductivities, χ (Ω^{-1} cm^{-1}), of $LiSO_3CF_3 \cdot 2NH_3$ and $LiNO_3 \cdot 2NH_3$ for a series of temperatures are presented in Table 1.

The high conductivities (of the order of 10^{-2} Ω^{-1} cm^{-1} at ambient temperatures) are comparable with the best non-aqueous electrolytes [5];
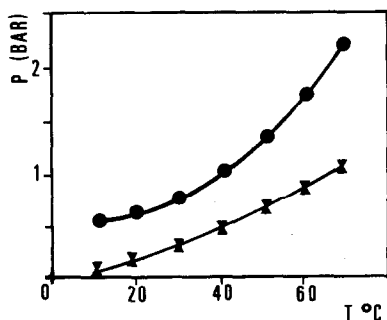

Fig. 1. Temperature dependence of NH_3 vapor pressure $p(NH_3)$ for $LiSO_3CF_3 \cdot 2NH_3$ (▼) and $LiNO_3 \cdot 2NH_3$ (●).

TABLE 1

Conductivities, χ, of $LiSO_3CF_3 \cdot 2NH_3$ and $LiNO_3 \cdot 2NH_3$

Temperature (°C)	Solvate	
	$LiSO_3CF_3 \cdot 2NH_3$	$LiNO_3 \cdot 2NH_3$
−15	0.51×10^{-3}	−
−10	0.65×10^{-3}	−
0	0.83×10^{-3}	0.993×10^{-2}
10	0.13×10^{-2}	1.39×10^{-2}
20	0.196×10^{-2}	1.9×10^{-2}
30	0.29×10^{-2}	2.58×10^{-2}
40	0.42×10^{-2}	3.4×10^{-2}
50	0.59×10^{-2}	4.4×10^{-2}
60	0.81×10^{-2}	5.64×10^{-2}
70	1.1×10^{-2}	7.09×10^{-2}

at 20 °C the nitrate ammoniate had a conductivity of $2.5 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$, while at -10 °C the triflate ammoniate had a conductivity of $0.6 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$.

The variation of log (χ) with $(1/T)$ was linear (Fig. 2), within experimental error, and can be described by an Arrhenius-type relation:

$$\chi = A \exp - (E_c/RT)$$

where E_c is the activation energy for conduction. These energies were high (6.9 kcal mol^{-1} for $LiSO_3CF_3 \cdot 2NH_3$ and 5.6 kcal mol^{-1} for $LiNO_3 \cdot 2NH_3$), indicating a strong interaction between the ions and the NH_3 [3, 6]. The high viscosity of these ammoniates is further evidence for the presence of this strong interaction.

(iv) Electroactivity range

Cyclic voltammetry was used to determine the electroactivity range of the ammoniates. This range corresponds to the potentials which lie between those at which the oxidation peak current and the reduction peak current of the voltammogram increase. It is an important value because it is used when setting the maximum charging potential, and indicates whether the lithium electrode will behave reversibly in the battery. The electroactivity ranges for a lithium perchlorate ammoniate and for both ammoniates studied here are presented in Table 2. All potentials are with regard to the Li/Li$^+$ couple.

For the triflate and nitrate ammoniates, the reduction of Li$^+$ and the subsequent reoxidation of the deposited Li metal occurs at potentials near to OV, indicating that lithium is behaving quasi-reversibly.

NH_3 oxidation for $LiSO_3CF_3 \cdot 2NH_3$ occurs at potentials above 3.8 V (versus Li/Li$^+$). If the scanned potential limits are between 0 and 3.8 V (versus Li/Li$^+$), no reduction or oxidation peaks are observed. Virtually identical behavior was observed for the $LiNO_3 \cdot 2NH_3$ except that the anodic limit was 3.5 V.

(v) Reactivity with lithium metal

Lithium metal stored at room temperature in $LiNO_3 \cdot xNH_3$ or $LiSO_3CF_3 \cdot xNH_3$ ($1.6 < x < 2.5$) for 48 h underwent no dramatic changes, despite
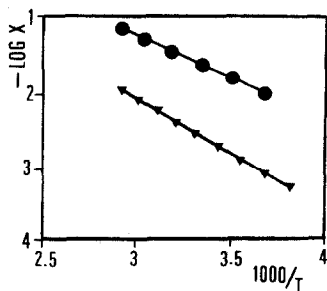

Fig. 2. Ionic conductivity as a function of temperature for $LiSO_3CF_3 \cdot 2NH_3$ (▼) and $LiNO_3 \cdot 2NH_3$ (●).

TABLE 2

Electrochemical window of various ammoniate electrolytes at room temperature on a Pt working electrode

Salts	E cathodic (V)	E anodic (V)
$LiSO_3CF_3$	0	3.9
$LiNO_3$	0	3.5
$LiClO_4$ (This electrolyte was reported in ref. 2)	0	3.7

the fact that nitrate is an oxidant. The shiny lithium surface acquired a dull grey film, which consisted of a passivating layer of $LiNH_2$ (by X-ray analysis). The mechanism contributing to the formation of the amide is probably similar to that for lithium metal in $LiClO_4 \cdot x NH_3$.

$$Li + NH_3 \longrightarrow LiNH_2 + 1/2H_2$$

No further changes, such as darkening, were observed for a period of three months, indicating that the passivating film prevented the lithium metal from reacting further with the electrolyte.

(vi) Manufacture of Li/MnO$_2$ batteries

Lithium batteries were constructed using the ammoniates, a lithium electrode, and an MnO_2 electrode (82% MnO_2, 3% PTFE, and 15% graphite deposited on a nickel foam). As the battery was discharged through a 1 kΩ resistor, a plot of the current as a function of time was recorded. At the end of the current plateau (corresponding to the end of the duty cycle; $V = 2$ V) the number of Faradays exchanged per mole of the cathode material, MnO_2, was 0.8 (charge passed was determined by integration of the current–time curve). The current–time curves for the nitrate ammoniate and the triflate ammoniate electrolytes were similar in shape to those for the $LiClO_4 \cdot x NH_3$ electrolyte [2] except that for the former two the plateau lengths were twice as long. See Fig. 3 where the discharge curves for the $LiClO_4 \cdot 4NH_3$ and triflate ammoniates are presented. With the triflate ammoniate the smaller current is due to the viscosity of the electrolyte. A theoretical gravimetric energy-density of approximately 650 W h kg^{-1} could be calculated for the Li/MnO$_2$ batteries made from the nitrate or triflate ammoniates. For the calculation of the theoretical gravimetric energy-density, only the necessary number of moles of MnO_2 and Li (with 0.8 Li for 1 MnO_2) has been considered. Thus, we did not take current collectors, separator, etc. into account.

Conclusions

Lithium nitrate ammoniate ($LiNO_3 \cdot 2NH_3$) and lithium triflate ammoniate ($LiSO_3CF_3 \cdot 2NH_3$) are very conductive electrolytes with low NH$_3$ vapor pres-
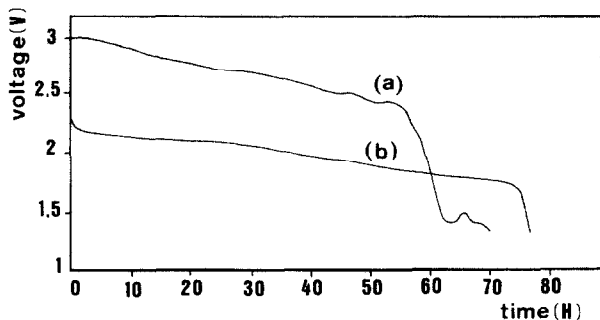
Fig. 3. Discharge curves at 20 °C of cells containing: (a) 6.46×10^{-3} mol MnO_2 cathode, $LiClO_4 \cdot 4NH_3$ electrolyte, and anode of pure Li; (b) 6.86×10^{-3} mol MnO_2 cathode, $LiSO_3CF_3 \cdot 2NH_3$ electrolyte, and anode of pure Li.

sures. From a safety point of view, the low NH_3 pressures ($p(NH_3) < 1$ bar at 50 °C) are a significant improvement. The lithium corrosion rate is very low for a wide temperature range. Hence, these ammoniates (especially $LiCF_3SO_3 \cdot 2NH_3$) can be employed as electrochemical generator electrolytes in lithium-based batteries.

Work is now in progress to lower the freezing point of the triflate ammoniate by mixing it with other ammoniates.

Acknowledgements

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