

## INFLUENCE OF WATER ADDITION ON STRUCTURAL AND ELECTROCHEMICAL BEHAVIOUR OF LIQUID AMMONIATES: A STUDY OF $\text{LiClO}_4 \cdot 4\text{NH}_3$ AMMONIATE/ $\text{H}_2\text{O}$ MIXTURES

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### Summary

The ammoniates of lithium perchlorate ( $\text{LiClO}_4 \cdot x\text{NH}_3$ ) can be used as liquid or solid electrolytes in lithium batteries. The compounds possess a very low ammonia pressure and a large electroactivity range at room temperature. The presence of water in the electrolyte is one of the main problems for the lithium anode. From calorimetric measurements on the water-ammoniate system and an X-ray powder diffraction study on crystalline compounds that appear on lithium dipped in the electrolyte, a maximum water content,  $x = 0.2$ , can be derived. Above this limit, the thermodynamic properties of the compounds change and the lithium reacts dramatically with the electrolyte. Electrochemical stability ranges behave, over all the water molar fractions studied, in accordance with structural features.

### Introduction

The ammoniates of some lithium salts,  $\text{LiClO}_4 \cdot x\text{NH}_3$ , can be used as liquid or solid electrolytes for lithium batteries. In particular, liquid ammoniates of lithium perchlorate,  $\text{LiClO}_4 \cdot x\text{NH}_3$ , possess a low  $\text{NH}_3$  pressure (<100 kPa) at room temperature, an appreciable ionic conductivity at 298 K ( $\sigma_{\text{LiClO}_4 \cdot 4\text{NH}_3} = 3.33 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$ ) and a large electroactivity range (more than 3.3 V). These features make such compounds very attractive for lithium batteries. High performance batteries have been tested with  $\text{LiClO}_4 \cdot 4\text{NH}_3$ , e.g., Li/CuO:2.6 V; Li/ $\text{MnO}_2$ :3.2 V; Li/(SN)<sub>x</sub>:2.8 V; all at room temperature [1, 2].

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The ammoniates are prepared with carefully dried salts and anhydrous  $\text{NH}_3$ , but the main problem is the possible presence of water in the electrolyte, because anhydrous ammoniates are very hygroscopic; water reacts vigorously with lithium and decreases the battery performance. Because of this problem, an attempt has been made to determine the action of water in the liquid ammoniate of lithium perchlorate when  $x = 4$ . In particular, a study has been conducted on the binary water-ammoniate system using isothermal microcalorimetry to highlight variations in the thermodynamic properties of the ammoniate when water is added. The phases formed at 298 K on lithium have been determined by qualitative X-ray diffraction (XRD) analysis. Finally, an investigation has been undertaken on the influence of water content on the electrical ( $\sigma$  at 298 K) and electrochemical properties of ammoniate electrolytes for lithium batteries. All preparations have been conducted under an argon-controlled atmosphere; residual water and oxygen, monitored with a hygrometer and an oxygen analyser, did not exceed 2 volumes per million.

## Experimental

### *Thermodynamic properties of ammoniate-water mixtures*

The molar enthalpies of mixing ( $\Delta H_M$ ) of a large number of mixtures of  $\text{LiClO}_4 \cdot 4\text{NH}_3 - x\text{H}_2\text{O}$  (water molar fraction range varying from  $x = 0$  to  $x = 0.35$ ) have been investigated. The object was to determine the partial molar heat variations ( $\Delta h_i$ ) of the components  $\text{LiClO}_4$ ,  $4\text{NH}_3$  and  $\text{H}_2\text{O}$  according to the relations:

$$\Delta h_{\text{ammoniate}} = \Delta H_M - x \left( \frac{d\Delta H_M}{dx} \right)$$

and

$$\Delta h_{\text{water}} = \Delta H_M + (1 - x) \left( \frac{d\Delta H_M}{dx} \right)$$

The enthalpies of mixing were determined by means of a Setaram micro calorimeter (Calvet type) [3]. The isothermal temperature was kept constant at  $298 \pm 0.05$  K.

### *Lithium stability in ammoniate-water mixtures*

X-ray diffraction was employed to identify the solid-state chemical species formed on lithium metal after 6 months in different ammoniate-water mixtures at 298 K. Powder diffraction patterns of crystalline compounds detected on lithium were recorded under a controlled atmosphere using nickel filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ).

### Conductivity and electroactivity ranges of $\text{LiClO}_4$ ammoniate–water system

The conductivities were determined by impedance measurements at 1 kHz, using a glass cell with smooth platinum electrodes. The redox stability ranges were obtained by cyclic voltammetry on a smooth platinum electrode (area:  $0.18 \text{ mm}^2$ ).

### Results and discussion

Figure 1 presents  $\Delta h_{\text{ammoniate}}$  and  $\Delta h_{\text{water}}$  (at 298 K) as functions of the water molar fraction ( $x$ ) in the system. The most striking feature of the curves is the well-resolved step that occurs at a water molar fraction of  $x \cong 0.2$ . For  $x < 0.2$ , the partial molar heat of the ammoniate remains roughly constant (i.e.,  $\Delta h_{\text{amm.}} \cong -100 \text{ mJ}$ ) and at a value that is much smaller than that for water (i.e.,  $\Delta h_{\text{amm.}}/\Delta h_{\text{water}} \cong 1/50$ ). In fact, it may be probable that water addition in this range does not produce any major modification in the initial thermodynamic properties of the liquid anhydrous ammoniate.

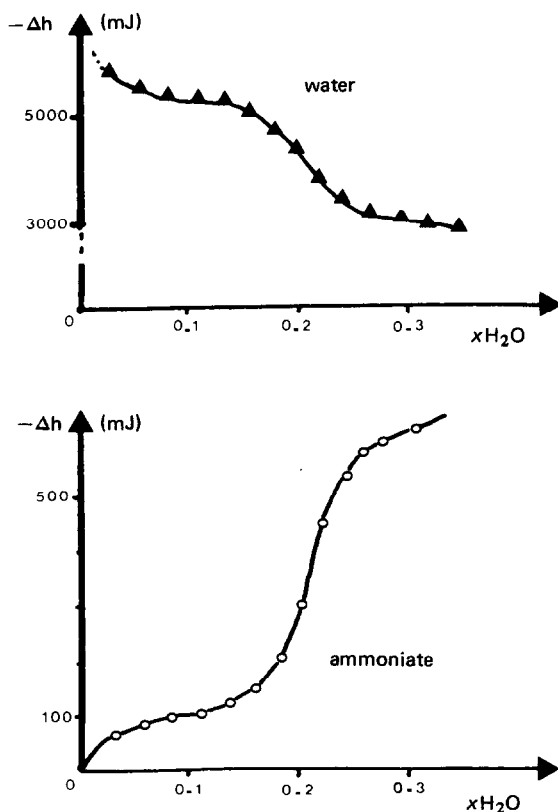


Fig. 1. Partial molar heats of ammoniate and water in  $(1-x) \text{LiClO}_4 \cdot 4\text{NH}_3/x\text{H}_2\text{O}$  system at 298 K.

The distinct step occurring at 0.2 suggests that the interactions between the ammoniate and water are different, depending on whether water molar fractions are smaller or greater than 0.2. Water additions in the higher range cause significant modification of the thermodynamic properties of the ammoniate.

X-ray diffraction analysis of lithium immersed in ammoniate-water mixtures gave the following results.

(i) Only  $\text{LiNH}_2$  phase could be observed on lithium metal dipped in  $\text{LiClO}_4 \cdot 4\text{NH}_3$  anhydrous ammoniate; the metal was covered by an amide film.

(ii) In the water molar fraction range  $0 < x < 0.2$ , the lithium metal was covered by a crystalline compound film in which a crystalline  $\text{LiNH}_2$  phase predominated together with a small amount of hydroxide.

(iii) For a water molar fraction  $> 0.2$ , the lithium metal reacted totally with water; the mixture consisted essentially of a crystalline  $\text{LiOH}$  phase.

In the water molar fraction range studied, the conductivity enhancement is due to the effects of the high dielectric constant of water, and especially to the lower hydrated electrolyte viscosity ( $\eta_{\text{anhydrous}} = 21.5 \text{ cP}$  and  $\eta_{\text{hydrated } x = 0.2} = 18.5 \text{ cP}$  at 298 K). The conductivity increases more rapidly in the lower water molar fraction range ( $\sigma_{x=0} = 8.5 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$  to  $\sigma_{x=0.15} = 12 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ ) than in the higher one ( $\sigma_{x=0.3} = 13 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ ). In the higher molar fraction range ( $x > 0.15$ ), con-

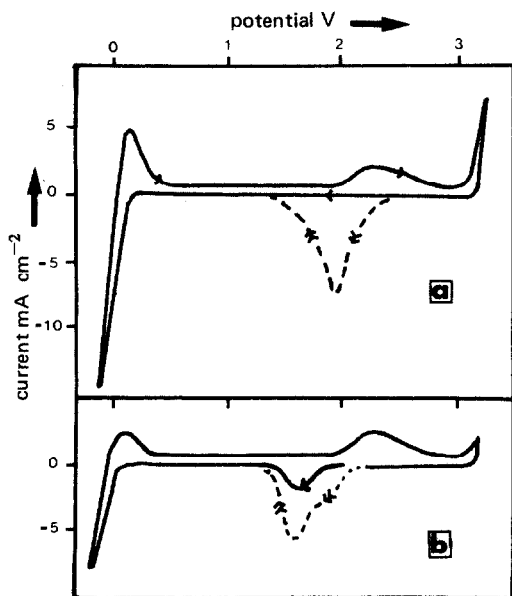


Fig. 2. Cyclic voltammograms of (a) anhydrous ammoniate  $\text{LiClO}_4 \cdot 4\text{NH}_3$ ; (b) hydrated ammoniate  $0.95 \text{ LiClO}_4 \cdot 4\text{NH}_3 - 0.05 \text{ H}_2\text{O}$ .

ductivity modifications produced by water addition are less effective; this demonstrates that the relative viscosity variation is not important.

The electrochemical stability window of the anhydrous ammoniate of lithium perchlorate lies in the potential interval 0 - 3.3 V. The electroactivity range is limited by lithium deposition in the cathodic region, and by ammonia oxidation into  $\text{NH}_4^+$  and  $\text{N}_2$  in the anodic region (Fig. 2). During anodic to cathodic polarization at +2 V (*versus* Li/Li<sup>+</sup>),  $\text{NH}_4^+$  reduction into  $\text{H}_2$  and  $\text{NH}_3$  occurs. In this region, for a cathodic to anodic polarization, an oxidation of  $\text{NH}_2^-$  appears.

For slightly hydrated ammoniate ( $x \cong 0.05$ ), the stability range is shortened; only the cathodic process changes (Fig. 2). A water reduction wave occurs at about +1.9 V (*versus* Li/Li<sup>+</sup>) and a slight increase is also observed in anodic current. The water wave reduction increases with the water molar fraction in the range  $0 < x < 0.2$ . For  $x > 0.2$ , lithium reacts vigorously with water.

## Conclusion

Electrical measurements and structural investigations of the anhydrous and hydrated ammoniate electrolytes  $(1 - x) \text{LiClO}_4 \cdot 4\text{NH}_3 - x\text{H}_2\text{O}$  ( $0 < x < 0.4$ ) reveal the following:

- in the low water molar fraction range ( $0 < x < 0.2$ ), thermodynamic properties of hydrated and anhydrous solvent are almost identical; in this interval lithium reacts preferentially with ammonia;

- in the high water molar fraction range ( $x > 0.2$ ), the thermodynamic properties of the ammoniates are different from those of the anhydrous solvent; in this interval lithium reacts totally with water;

- the water molar fraction  $x = 0.2$  is associated with the dehydration limit in the preparation of anhydrous electrolyte; lithium metal cannot completely dehydrate hydrated ammoniates;

- conductivity and electrochemical stability ranges behave, over all the water molar fraction studied, in accordance with structural features; these properties are different according to whether water molar fractions are higher or lower than  $x = 0.2$ .

This behaviour of lithium in  $\text{LiClO}_4 \cdot 4\text{NH}_3$  ammoniate seems to be general: below a certain water concentration, alkali metals do not react with water in liquid ammoniates. This has also been observed with sodium. At room temperature, sodium in contact with the liquid ammoniate of sodium iodide,  $\text{NaI} \cdot 3.3\text{NH}_3 \cdot x\text{H}_2\text{O}$ , does not react with water if  $x < 0.1$ . Such behaviour of alkali metals indicates that ammoniates hold little promise as new electrolytes for powerful batteries.

## References

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