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# Physical-Chemical and Electrochemical Studies of the Lithium Naphthalenide Anolyte

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ABSTRACT

We carried out physical-chemical and electrochemical characterizations of lithium naphthalenide solutions in tetrahydrofuran (THF) in view of their potential use as liquid anode material in rechargeable batteries. Concentrations of dissolved naphthalene and lithium were varied to prepare homogeneous solutions of general formulae $Li_xN(THF)_n$; $0 \leq x \leq 2$ and $3 < n < 25$. FTIR investigations support a two-step mechanism for $Li_xN(THF)_n$ formation. For $0 < x < 1$ the solutions consist of mixture of lithium-free naphthalene $Li_0N(THF)_n$ and lithium-bound naphthalene $Li_1N(THF)_n$ whereas for $1 < x < 2$ the solutions consist of mixture of $Li_1N(THF)$ and $Li_2N(THF)_n$ solutes. Electrical conductivity traces ($\sigma(x, n)$) make a maximum at $x \sim 1$ in diluted solutions ($n > 10$) and at $x \sim 0.5$ for more concentrated ones ($n < 10$). The highest $\sigma$ value of 12.4 mS/cm is achieved in $Li_{0.5}N(THF)_{6.2}$ composition. The conductivity of $Li_xN(THF)_{10.4}$ solutions shows linear behaviour with temperature of with negative slopes highlighting its metal-like character. We found a logarithm law of viscosity with ‘x’, a common feature in amorphous systems.

Entropy and enthalpy measurements were performed in a Li/Ceramics/$Li_1N(THF)_{10.4}$ half-cell by monitoring open-circuit potentials (OCP) changes in the temperature range of 25 °C – 10 °C. A full cell consisting of $Li_1N(THF)_{10.4}$ anode and a iodine based liquid cathode was successfully tested to proof the concept of a new all liquid electrodes refillable lithium batteries.

## 1. INTRODUCTION

Lithium naphthalenide is usually prepared by the alkali metal dissolution in a solution of naphthalene in an ethereal solvent such as tetrahydrofuran (THF) and dimethoxyethene (DME). The Li 2s electron is transferred to the poly-aromatic hydrocarbon molecule (PAH) naphthalene $\pi$-orbital and the so-formed complex is stabilized by solvation. Because of this particular structure, lithium naphthalenide is also known to as a “solvated electron solution” (Li-SES) in which lithium is the charge compensating cation. The solvated electron in Li-SES is not involved in any strong bonding, which makes it available for charge transportation and for chemical reactions. In fact, as for other alkali metal naphthalenides, lithium naphthalenide is known for its strong reducing character and it is commonly used as reductant in organic, organometallic and inorganic chemistry [1–6] and as initiator in anionic polymerization [7–11]. One of the characteristics of lithium naphthalenide is its more or less dark green colour arising from the presence of radical anions and di-anions according to Li/naphthalene ratio and THF content. For convenience lithium naphtalenide solutions will be represented here by the overall formulae $Li_xN(THF)_n$, N = naphthalene.

In this work $Li_xN(THF)_n$ solutions were prepared in the composition range of $0 \leq x \leq 2$ and $3 \leq n \leq 25$. The solutions were then characterised by FTIR, electrical conductivity, viscosity and open-circuit voltage (OCP) measurements. The FTIR data analysis support a “two-phase” model in which the solutions consist of $Li_0N(THF)_n + Li_1N(THF)_n$ and of $Li_1N(THF)_n + Li_2N(THF)_n$ mixtures in the composition ranges of $0 \leq x \leq 1$ and of $1 \leq x \leq 2$, respectively.

Preliminary electrochemical tests support the concept of refillable lithium battery in which both anode and cathode are in a liquid state.

## 2. EXPERIMENTAL

### 2.1. $Li_xN(THF)_n$ solutions preparation

$Li_xN(THF)_n$ solutions were prepared in an argon-filled glovebox at ambient temperature. Metallic lithium foils, anhydrous THF and naphthalene were obtained from Sigma Aldrich. The preparation proceeded via the following steps:

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i Well defined amounts of THF, naphthalene and Li are measured out separately to achieve a target composition of $0.50 \leq x \leq 2.00$ and $3 \leq n \leq 25$.
ii First, naphthalene is dissolved in THF in a glass bottle to form a transparent, colourless solution of well defined 'n' in $Li_0N(THF)_n$.
iii Second, Li foils are added to the above solution and the bottle was sealed.
iv The mixture is stirred overnight using a glass-coated magnetic bar.

The so formed $Li_xN(THF)_n$ solutions colour ranges from blue to dark green according to x and n values. The volume expansion vs. the amount of naphthalene dissolved in step ii. was monitored.

An identical procedure was applied to prepare lithium-biphenyl (β) solutions ($Li_x\beta(THF)_n$) for comparative studies purposes [12].

### 2.2. FTIR characterization

The FTIR Spectra of the $Li_xN(THF)_n$ solutions were obtained using a Shimadzu IRPrestige-21 and a Perkin Elmer Frontier operated in the absorbance mode which better accounts for the solutions concentration. Details on FTIR sample preparation and measurements procedure are given in [12].

### 2.3. Viscosity Measurements

Viscosity of the $Li_xN(THF)_{10.4}$ solutions (x = 0.5, 1, 1.5 and 2), was measured at ambient temperature using a portable Viscolite 700-T15 Small Sample Viscometer inside a glovebox filled with argon.

### 2.4. Conductivity measurements

Ambient temperature conductivity measurements were performed on $Li_xN(THF)_n$ (x = 0, 0.5, 1, 1.5 and 2; n = 5.23, 6.18, 6.99, 9.27, 12.9, 24.1) in a glove box filled with argon. A TetraCon 325 Standard conductivity cell probe with a measurement range of 1 μS/m to 2 S/cm is used. The probe was attached to a Cond3310 meter based on the four-electrode technique.

For conductivity vs. temperature T measurements the bottle containing the $Li_xN(THF)_{10.4}$ sample with x = 0.5, 1, 1.5 and 2 was sealed inside the glove box by wrapping it with para-film and then the bottle was taken out and immersed in a container filled with dry ice. The bottle was cooled down to ~8 °C then it was transferred back into the glove box. The bottle was unsealed and the liquid sample was transferred into an insulated container. The conductivity of the $Li_xN(THF)_{10.4}$ sample was then measured as its temperature slowly rose to the ambient temperature, which takes one and two hours allowing quasi isothermal conductivity measurements to be performed.

### 2.5. OCP, entropy and enthalpy measurements

OCP measurements were performed on an H-shape half-cell with two compartments hermitically separated by a Li-ion conducting ceramic membrane produced by Ohara, Japan. $Li_xN(THF)_{10.4}$ solution is placed in the first compartment and a nickel mesh attached to a nickel wire is used as the current collector. In the second compartment metallic lithium pressed on a nickel grid attached to a nickel wire is immersed in a 1 M $LiPF_6$ in EC: DEC electrolyte solution. Metallic lithium serves as the reference and the counter electrode in the cell. The later can be schematically described by the chain:

(+) Ni/ $Li_{1.0}N(THF)_{10.4}$/ Ceramics membrane/ Li, 1 M $LiPF_6$ in EC: DEC/Ni (−)

The cell was placed into an ESPEC PR-1FP Temperature & Humidity Chamber for OCP vs. T measurements operating in the $10\,^{\circ}C \leq T \leq 25\,^{\circ}C$ range using an APPA 505 True RMS digital multimeter cum data-logger. Entropy and enthalpy data are computed from the temperature dependence of OCP.

## 3. RESULTS

### 3.1. Volume expansion

During step ii. of Section 2.1, the solution volume expends linearly with the relative amount of dissolved naphthalene (i. e. $\frac{1}{n}$) following the Equation:

$$\frac{\Delta V}{V_0} = \frac{1.375}{n} \qquad (1)$$

Eq. (1) is valid up to the solution saturation when 3.6 moles of naphthalene per litter of THF are dissolved. Accordingly, the relationship between naphthalene concentration 'c' (mole/l) and

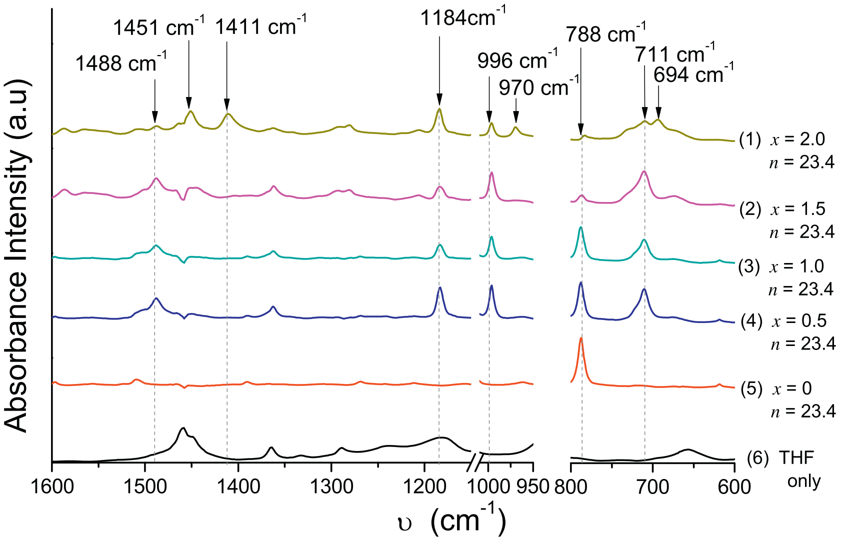

**Fig. 1.** FTIR Spectra of pure THF and of $Li_xN(THF)_{23.4}$, x = 0, 0.5, 1, 1.5, and 2 in the 1600 cm$^{-1}$ to 600 cm$^{-1}$ frequency range.