

New Potential Candidates for Redox Battery Using Liquid Ammoniates: Na^+/Na and Ag^+/Ag

Anne-Marie Gonçalves,^{a)*} Pierre Tran-Van,^{a)} Guillaume Herlem,^{b)} Edith
Kwa,^{b)} Bernard Fahys,^{b)} Michel Herlem^{a)}

^{a)} IREM-CNRS, Institut Lavoisier, Université de Versailles St-Quentin-en-Yvelines, 78035
Versailles Cedex, France

^{b)} LCMI, Université de Franche Comté, 16, route de Gray, La Bouloie, 25030 Besançon,
France

Received 29 April 2005; accepted in revised form 19 October 2005

Abstract

Liquid ammoniates, which are highly conductive electrolyte (more than $100 \text{ mS}\cdot\text{cm}^{-1}$ at 20°C), are proposed as solvents for a redox battery working around room temperature, and up to 80°C . In the negative compartment, the anolyte is $\text{NaI} \cdot 3.3\text{NH}_3$, and the Na^+/Na couple is proposed. It is reversible, as determined by cyclic voltammetry and galvanostatic cycling.

In the positive compartment, the catholyte $\text{NaI} \cdot 3.3\text{NH}_3$ enriched in silver cations is proposed too. The cathodic material is merely this compound and the cathode is the silver metal. The couple Ag^+/Ag is reversible too, as determined by cyclic voltammetry and galvanostatic cycling.

Metallic sodium is extremely stable in this electrolyte; therefore $\text{NaI} \cdot 3.3\text{NH}_3$ could be used in a redox battery of high energy density and high power density. The maximum working temperature, which is proposed, 70°C , is lower than the melting point of sodium (98°C), and avoids high pressures of ammonia.

Keywords: rhodium microparticles, electrocatalysis, carbon monoxide, formic acid, FTIR study.

Introduction

Oxidation of small organic molecules on bulk noble metals has been extensively studied [1]. Recently, some researchers have been dealing with highly dispersed metal microparticles on graphite, glassy carbon, as well as on conducting polymer films [2-9], by reduction of metal ions with consecutive potential cycling as the favourite method suitable for the desired electrodeposition. Platinum microparticles have been used for the electrooxidation of carbon

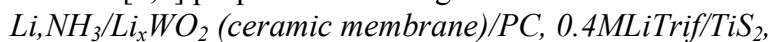
* Corresponding author. E-mail address: gonalvalve@chimie.uvsq.fr

monoxide, methanol and formic acid [5, 6, 8, 9], while palladium microparticles were used for electrooxidation of CO [8], and gold microparticles for oxidation. Here we propose to use as anodic material, solid sodium, in large excess, and to use as cathodic material silver iodide. During the discharge, the sodium anode yields Na^+ ions, while Ag^+ ions are reduced to Ag at the silver cathode. During the charge Na^+ ions yield sodium while Ag yields Ag^+ ions. Sodium iodide as well as silver iodide gives liquid ammoniates at room temperature under a low ammonia pressure [1]. For sodium iodide, the addition compound between NaI and NH_3 , $\text{NaI} \cdot x\text{NH}_3$ is liquid for $3 < x < 3.5$.

The electrochemical window of the electrolyte is 2.5 V, and is rather low when compared to the well-known carbonates such as propylene carbonate. However, to date no electrolyte is disadvantage-free: $\text{NaI} \cdot 3.3\text{NH}_3$ provides major advantages, namely high conductivity and high chemical compatibility with sodium. Here we chose to use Pt as backing material for sodium deposition, but other metals less expensive than Pt could be used (copper, nickel).

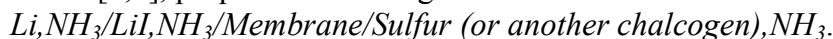
At low temperature ($T < -33\text{ }^\circ\text{C}$), alkali metal/alkali cation redox couples in liquid ammonia are completely reversible at a smooth platinum and at a smooth gold electrode. Although all alkali metals are soluble in large amounts in liquid ammonia [1], up 16 M, leading thus to discharges, electrochemical cells which have a negative electrode (anode) including an alkali metal dissolved in liquid NH_3 , have been proposed and patented. These inventions were used in the field of reversible high-power electric cells operating at low temperatures.

Sammels *et al.* [2,3] proposed the configurations:



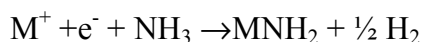
Thus, the positive material is dipped in a non aqueous solvent, different from ammonia, e. g., propylene carbonate [2], SO_2 [2], and also 2-methyltetrahydrofuran [3]; supporting electrolyte: LiCF_3SO_3 or LiAsF_6 .

Lelieur *et al.* [4,5], proposed the configuration:



Concentrated lithium iodide solution in NH_3 leads to the demulsibility of the Li, NH_3 phase, avoiding thus the contact of solvated electrons with the membrane, which can be consequently made of many materials chemically compatible with ammonia.

All cells show reversibility and open circuit voltage up to 3.4 V with Li. Such cells need a separator, which must be efficient and chemically stable toward solvated electron on the one hand, and the chemical stability of alkaline metals in solution in liquid ammonia during long periods is an important problem which has not been solved on the other hand, although the purification of the alkali metals improves the stability, since the impurities catalyze the formation of amides,



This is why no commercial solvated electron battery has been made until now.

At room temperature a solvated electron battery would be hazardous since the ammonia pressure could be very high (up to 7 bars) and since the decomposition reaction of ammonia into amides could take place quickly in the presence of impurities, such as metallic oxides and hydroxides, yielding high amounts of hydrogen [6].

This is why we investigated the electrochemical behavior of sodium, in the liquid ammoniate $\text{NaI} \cdot 3.3\text{NH}_3$. This liquid ammoniate looks like a fused salt, and since the concentration of sodium ions is very high, 7 M, the formation of the solvated electron does not occur. This allows the use of solid sodium as anode. We proposed already this metal as anode for primary batteries [7,8], but we did not check the possible reversibility of Na^+/Na , in anhydrous conditions as well as in the presence of water traces.

Alkali metals are very electropositive, which makes them good materials as negative electrodes for high energy density batteries. However, they present in general several drawbacks, mainly: high reactivity with liquid electrolytes and low cyclability (for example due to dendrite growth). Lithium is very reactive but has the highest specific capacity of all alkali (3860 mAh.g^{-1}), so it is the most studied.

Sodium has less specific capacity than lithium, (1166 mAh.g^{-1}), but is nevertheless a good candidate for a battery, especially considering the fact that so far, the theoretical capacity of lithium has not been exploited. Na has been studied for a few batteries with liquid electrolytes such as DME with NaPF_6 or NaClO_4 in PC [9]. Solid electrolytes were tested with liquid sodium for high temperature primary batteries [10]. Several compounds have a structure admitting Na^+ intercalation or displacement reactions, such as sulfur [11,12] chalcogenides (TiS_2 [13], $\text{TaFe}_{1.25}\text{Te}_3$ [14], vanadium bronzes [15], phosphomolybdates [16], cobalt oxides [17], polymers [18], NiCl_2 [19]). To our knowledge, no commercial secondary batteries using sodium exist (even if prototypes such as ZEBRA batteries are in development $\text{Na}/\text{NaAlCl}_4$ in $\beta''\text{-Al}_2\text{O}_3/\text{NiCl}_2$ [20,21,22]).

Obviously, the issue of conductivity and temperature can be avoided with a liquid electrolyte, to the detriment of reactivity with Na. However, one ammonia-based electrolyte combines all the advantages and none of the drawbacks of liquid and solid electrolytes, which is $\text{NaI} \cdot 3.3\text{NH}_3$. Since I^- is not reducible, sodium metal is extremely stable in this electrolyte and keeps a shiny surface for months, provided the electrolyte is pure enough [23]. Moreover, the ionic conductivity is very high, e.g. 103 mS.cm^{-1} at 20°C . For a working temperature, inferior to 70°C , lower than the melting point of sodium (98°C), high pressures of ammonia can be avoided (only 2 bars at $T = 70^\circ\text{C}$).

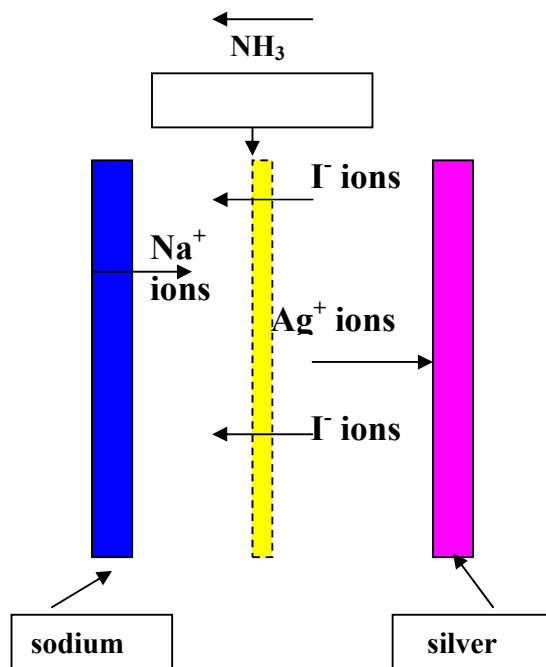
Lithium halides are not very soluble in NH_3 and do not yield liquid ammoniates at room temperature under a low ammonia pressure. Consequently, lithium, which can reduce all other anions, is not stable in other ammoniates [24]. This is why this paper deals with the use of $\text{NaI} \cdot 3.3\text{NH}_3$ as anolyte in the negative compartment with sodium as anode. Recently, this ammoniate has been successfully used in electrochromic devices [25]. Although sodium has already been proposed as an anode in primary batteries [7,8], its reversibility has not

been studied. Here we studied its reversibility in anhydrous conditions, and in the presence of water. The purpose is to finalize a redox battery whose sodium anode could be prepared by sodium deposition before the first use, thus avoiding the setting up of sodium electrodes which can be difficult and hazardous.

The potential window of ammoniates containing Γ anions is inferior to 3 V, a value which needs a positive electrode with a redox potential about +2 V/Na. It is why we chose as positive electrode the couple Ag^+/Ag . Ag^+ ions are very soluble in liquid ammonia, and in $\text{NaI} \cdot 3.3\text{NH}_3$. AgI gives also a liquid ammoniate at room temperature [26]. Here we studied solutions of AgI up 1M.

When the composition of the ammoniate $\text{NaI} \cdot x\text{NH}_3$ changes, the pressure changes too. If x increases, $p(\text{NH}_3)$ increases. If x decreases, $p(\text{NH}_3)$ decreases. It is easy to equalize the pressures by a valve between the anolyte and the catholyte compartments during charge and discharge cycles. See the scheme of the redox battery.

Only the Na/Na^+ and the Ag^+/Ag redox couples are studied here.



Discharge

Scheme of the redox battery during discharge.

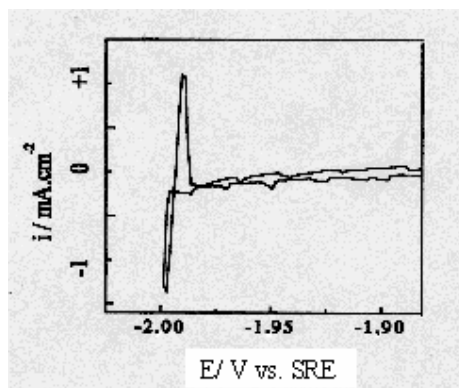


Figure 1. Cyclic voltammogram with a current threshold of $1 \text{ mA}\cdot\text{cm}^{-2}$ corresponding to stationary state in anhydrous conditions. Smooth Pt electrode.

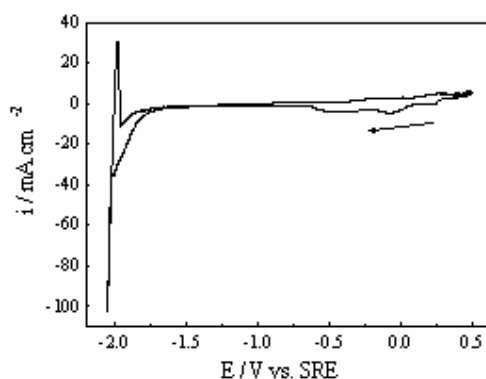


Figure 2. Cyclic voltammogram with a current threshold of $100 \text{ mA}\cdot\text{cm}^{-2}$, in the presence of a large added amount of water (10^{-2} M). Reduction of Na^+ to Na occurs at about -2 V/SRE . Smooth Pt electrode.

Experimental

Electrolyte synthesis and purification

The liquid ammoniate was synthesized by condensing an excess of ammonia (Air Liquide, electronic quality) on NaI (dry NaI, Prolabo) at $-50 \text{ }^\circ\text{C}$. The resulting solution is colorless. The purification procedure involves the use of solvated electrons: metallic sodium was added in large excess referred to the estimated water concentration, essentially due to NaI. The blue color characteristic of solvated electrons immediately appeared. These electrons are strong reducing agents that reacted with impurities such as O_2 or H_2O , as well as excess NH_3 (yielding NaNH_2). After bleaching, this solution was warmed at $+20 \text{ }^\circ\text{C}$. After decanting the solution and pumping the excess of ammonia, the electrolyte was stored in a glove box. The chosen composition was $\text{NaI}\cdot 3.3\text{NH}_3$. The composition is easy to follow by successive weighing.

For AgI solutions in this liquid ammoniate, AgI additions were done in $\text{NaI}\cdot 3.5\text{NH}_3$, to obtain $\text{Ag/NaI}\cdot 3.3\text{NH}_3$. Ammonia was added if necessary.

Electrochemical measurements

Electrochemical measurements were performed with a potentiostat/galvanostat AUTOLAB PGSTAT20 (Ecochemie). For the study of the Na/Na⁺ couple, the working electrode was a disk of polished nickel or platinum (respectively 6 and 2 mm diameters); the counter electrode was a sodium sheet wrapped on a silver wire, and the reference electrode was a silver wire (SRE: Silver Reference Electrode). Cyclic voltammetry was typically performed with scans starting in reduction, with the onset of the reverse scan determined by a threshold in current. Galvanostatic cycling was performed with a cut-off value of 2.0 V and a charge density of 1 C.cm⁻². The coulombic efficiency Q_{eff} was recorded as a function of cycle number N . Q_{eff} is defined as the ratio of the charges measured during a single step of oxidation and reduction, respectively.

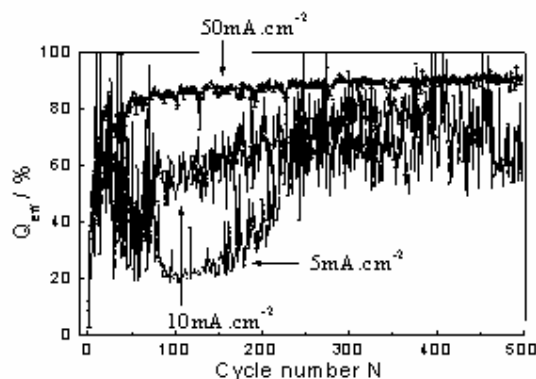


Figure 3. Coulombic efficiency Q_{eff} as a function of cycle number N , for different values of the current density i .

Results

1. Half-cell for a sodium secondary battery using sodium iodide liquid ammoniate as electrolyte

Na/Na⁺ couple. —Cyclic voltammetry.— Fig. 1 displays a cyclic voltammogram corresponding to stationary state, with a current threshold of 1 mA.cm⁻² in anhydrous conditions. Fig. 2 displays a cyclic voltammogram with a current threshold of 100 mA.cm⁻², in the presence of a large added amount of water (10⁻² M). Reduction of Na⁺ to Na occurs at about -2 V/SRE. Note that the upper potential was limited to 0 V in order to avoid oxidation of I⁻ ions, which occurs at about 0.5 V. During the reverse scan, an anodic current is immediately observed, even in the presence of water. Integration of both peaks reveals a ratio of coulombic efficiency equal to 1 in the absence of water, even for the low current threshold, and close to 0.97, accounting for the baseline, in the presence of water. The Na/Na⁺ couple therefore behaves reversibly in NaI•3.3NH₃.

Na/Na⁺ couple.—Galvanostatic cycling.— Galvanostatic cycling imposes more brutal perturbations at the electrode surface, which allow getting a clearer picture of the behavior of the Na/Na⁺ system in a real battery with the chosen electrolyte. In the absence of water, Q_{eff} is always equal to 1. In the presence of 10^{-2} M water, a very large amount, Fig. 3, shows the evolution of the coulombic efficiency Q_{eff} as a function of cycle number N , for different values of the current density i . As i increases, the shape of the curve becomes more and more erratic, but for high current densities, as soon as water is reduced, the deposition of sodium takes place. Since the volume of our cell is large, it leads to a large water reservoir and the H₂O reduction needs several cycles before sodium deposition can occur (see Fig. 3). The higher the current densities, the higher Q_{eff} .

These results mean that sodium could be deposited during the first charge cycle in anhydrous conditions, whatever the electrolyte volume would be. In presence of water traces, even for 10^{-2} M, for small electrolyte volumes, as soon as water is reduced, sodium can be deposited. In practical cells, the electrolyte volume is small since the electrolyte is located in the separators. In these conditions it is obvious that water could lead to a loss of capacity, but this impurity should be reduced during the first cycle and its presence does not prevent sodium deposition. Q_{eff} could be as high as 80% at $50 \text{ mA}\cdot\text{cm}^{-2}$. 70-80% yield only for the first charge cycle is typically an excellent value of coulombic ratio, when compared to Li cycling in PC, for example [27]. When possible, anhydrous conditions lead to 100% efficiency.

Discussion

Sodium has excellent chemical stability in $\text{NaI} \cdot 3.3\text{NH}_3$. This can be explained by the nature of the anion (I^- is not reducible) and by the structure of the electrolyte: the concentration of NaI is very high (6-7 M), and as a consequence the electrolyte has a structure akin to a molten salt. The plating of sodium does not imply any surface film formation, as is so often the case with lithium plating. Of course, neither moisture nor oxygen are present, and the iodide ions are known to strongly adsorb at electrode surfaces, thus avoiding reduction of NH_3 [28,29,30].

The Na^+/Na couple behaves quasi reversibly in the ammoniate-based electrolyte. Moreover, in the presence of water, the Na^+/Na couple presents an interesting feature: the coulombic efficiency rises when the current density is raised. In these experiments, the charge density is kept constant, so the higher is the current density, the shorter is the duration of a given step. However, in most systems a high current density is detrimental to cycling. This means this electrolyte could be well adapted for applications demanding high power output, at least from the point of view of conductivity and negative electrode.

2. Half-cell for a secondary battery using Ag/sodium iodide liquid ammoniate as electrolyte

Cyclic voltammetry

The voltammograms for $1 \text{ mV}\cdot\text{s}^{-1}$ are presented for two Ag^+ concentrations. See Fig. 4. One can see a hysteresis for the Ag^+ reduction: for the reverse scan, the

reduction of silver ions is easier. As soon as the Pt electrode is coated by silver, its electrochemical behavior is changed. The peak areas are almost identical.

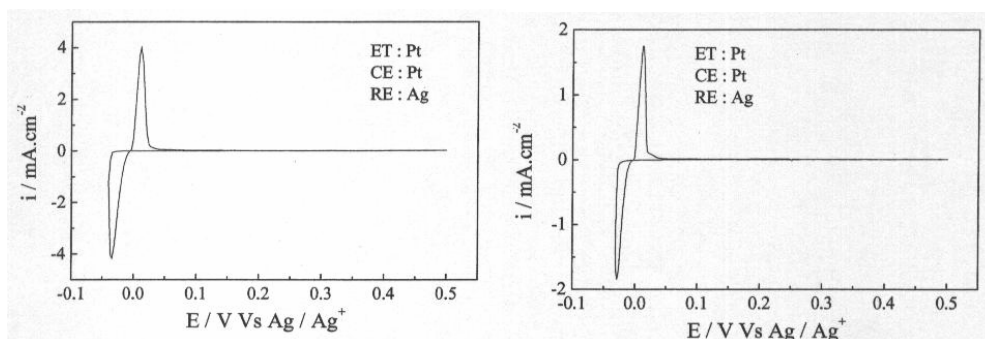


Figure 4. Current-tension curves for AgI in NaI • 3.3NH₃ for a scan rate of 1mV.s⁻¹. The sweep was stopped for $|i| > 1\text{mA}\cdot\text{cm}^{-2}$. WE : Pt, CE : Pt, RE : Ag. AgI concentration: (a) 1M, (b) 4M.

Chronopotentiometry

A typical chronopotentiogram is represented in Fig. 5. The deposition of silver leads to a plateau at -18 mV vs. SRE. During dissolution steps, the potential increased progressively from 3 to 34 mV. The overpotentials were symmetrical.

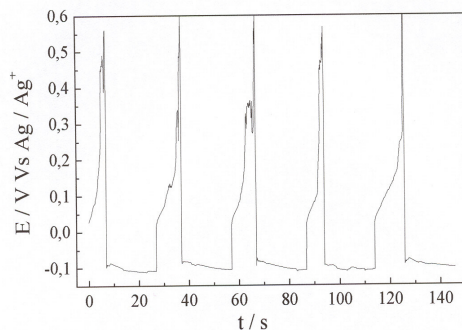


Figure 5. Chronopotentiogram of AgI + NaI, in NaI•3.3NH₃, for a AgI concentration of 1M, corresponding to cycles 21 to 25. WE : Pt, CE : Ag, RE : Ag. $Q_p = 1\text{C}\cdot\text{cm}^{-2}$, $Q_s = 1\text{C}\cdot\text{cm}^{-2}$, $E_{c(\text{ox})} = 0.5\text{V}/\text{RE}$, $i = 1\text{mA}\cdot\text{cm}^{-2}$.

Influence of the Ag⁺ concentration

The evolution of the faradic yield vs. the cycle number is represented on Fig. 6 for two Ag⁺ concentrations. The efficiencies become equal for less than 20 cycles. The yield which is obtained is good at a Pt electrode. Its evaluation is difficult at a silver electrode.

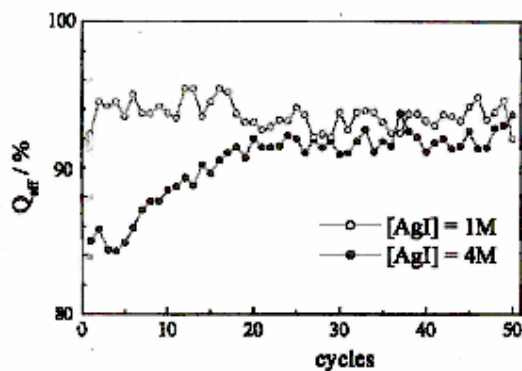


Figure 6. $Q_{\text{eff}} = f(N)$ curves for AgI in NaI • 3.3NH₃ for different concentrations in AgI. WE : Pt, CE : Ag, RE : Ag. $Q_p = 1\text{C.cm}^{-2}$, $Q_s = 1\text{C.cm}^{-2}$. $E_{c(\text{ox})}=0\text{.V}$. $i=1\text{mA.cm}^{-2}$.

Influence of the current density

Fig. 7 shows the results of the chronopotentiometric measurements for a current density of 50 mA/cm². The higher the current density, the higher the silver deposition efficiency. The over potential is only 5 times higher than for 1 mA/cm², but the curve $Q_{\text{eff}} = f(N)$ becomes erratic. This may be due to silver islands which grow on small areas.

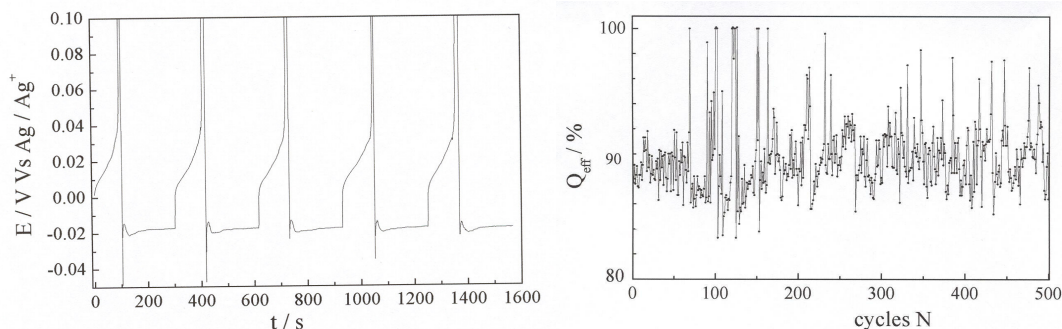


Figure 7. Cycling in AgI + NaI • 3.3NH₃ for a AgI concentration of 4M. WE : Pt, CE : Ag, RE : Ag. $Q_p = 1\text{C.cm}^{-2}$, $Q_s = 1\text{C.cm}^{-2}$. $E_{c(\text{ox})} = 0,5\text{V}$. $i = 50\text{mA.cm}^{-2}$. (a) curve $E = f(t)$ corresponding to cycles 51 to 55. (b) curve $Q_{\text{eff}} = f(N)$.

Discussion

The results of the cyclic voltammetry, and the results of galvanostatic cycles at a Pt electrode show a good reversibility of the Ag/Ag⁺ couple. The increase of deposition current density by 50 leads only to an over potential of 5: this indicates that the electrode interface is not perturbed. The coulometric efficiency is reliable. SEM observations show that the electrode surface is not homogeneous on Pt after deposition of Ag, while when a silver electrode is used the morphology is regular. This can explain that the efficiency is not close to 100% at a Pt electrode.

Conclusion

Compared with other redox batteries, the cell voltage, 2 V, is convenient but less than that obtained with the plurion zinc/cerium battery, which has a superior cell voltage (2.4 Volts). But $\text{NaI} \cdot 3.3\text{NH}_3$ is an electrolyte providing good ionic conductivity and excellent chemical stability with respect to sodium. The Na^+/Na could be used as active material for a sodium battery. So far it is the first time that an alkali metal leads to a fully reversible redox couple in any solvent except for molten salts. This behavior seems being due to the presence of high concentrations of sodium ions which prevent the sodium dissolution on one hand, and to the presence of high concentrations of iodide ions, on the other hand, that adsorb strongly on the sodium interface and prevent the formation of sodium amide. These properties allow the deposition of sodium on the anode before the first use, merely by cathodic reduction, thus avoiding the setting up of sodium electrodes, which can be hazardous. Our redox battery needs an anionic membrane, which is not yet found.

There are clear incentives to identify alternative electrochemical strategies which will permit long cycle life to be achieved in secondary batteries. We found that solid Na^+/Na system is fully reversible in the liquid ammoniate $\text{NaI} \cdot 3.3\text{NH}_3$. Discussed here is a new strategy which may be of merit for achieving higher reversibility in sodium based non aqueous cells. Although sodium has a molecular weight heavier than the one of lithium, its possible use as reversible solid anode material is interesting compared to Li. This last alkali metal reacts on all anions except halide anions (which are poorly soluble, e.g., Cl^- , F^- , or easily oxidized, e.g., Br^- , I^-) on the one hand, and yields dendrites and poor cycling efficiency during recharge steps on the other hand: it is used as intercalation compound, thus one loses the advantage of the low molecular weight of this metal. But the true advantage of Li is the high cell voltages which can be delivered, and consequently the high volume energy. This means that another advantage is needed for using sodium. Here this advantage is the very high conductivity of $\text{NaI} \cdot 3.3\text{NH}_3$. The use of silver salts leads too to a reversible system whose molar mass is less favorable, but although it is costly, it is not toxic.

References

1. See for example J. Jander, in «Anorganische und allgemeine Chemie in flüssigen Ammoniak», Friedr. Vieweg & Sohn, Interscience Publishers, Braunschweig, 1966.
2. A.F. Sammels, K.W. Semkov, *J. Electrochem. Soc.* 133 (1986) 1975.
3. F.A. Uribe, K.W. Semkov, A.F. Sammels, *J. Electrochem. Soc.* 136 (1989) 3559.
4. L. Bernard, J.-P. Lelieur, A. Le Méhauté, *US patent* 4,431,718, Feb. 1984.
5. L. Bernard, A. Demortier, J.P. Lelieur, F. t'Kint de Roodenbeke, A. Le Méhauté, *J. Phys. Chem.* 88 (1984) 3833.
6. W.L. Jolly and C.J. Hallada, in «Non-Aqueous Solvent Systems», T.C. Waddington, Editor, Chapter 1, Academic Press, Inc., London, 1965.

7. J. Badoz, M. Bardin, C. Bernard, M. Herlem, G. Robert, A. Thiébault, *J. Electrochem. Soc.* 135 (1988) 587.
8. J. Badoz, M. Bardin, C. Bernard, M. Herlem, G. Robert, A. Thiébault, US Patent , n° 4,446,215.
9. T.R. Jow, L.W. Shacklette, M. Maxfield, D. Vernick, *J. Electrochem. Soc.* 134 (1987) 1730.
10. K.M. Abrahams and L. Pitts, *J. Electrochem. Soc.* 128 (1981) 2574.
11. C.A. Vincent with F. Bonino, M. Lazzari and B. Scrosati, Edward Arnold Publishers, 168-203 (1984).
12. J.L. Sudworth, *J. Power Sources* 11 (1984) 143.
13. K.M. Abraham, *Solid State Ionics* 7 (1982) 199.
14. L. Sanchez, J.M. Tirado, C.P. Vicente, J.C. Jumas, *J. Solid State Electrochem.* 2 (1998) 328.
15. J.P. Pereira-Ramos, R. Messina, *Solid State Ionics* 40/41 (1990) 970.
16. L. Mesonero Herreo, M.E. Arroyo y de Dompablo, M.J. Ruiz Aragon and E. Moran, *J. Mater. Chem.* 8 (1998) 2405.
17. L.W. Shacklette, T.R. Jow, L. Townsend, *J. Electrochem. Soc.* 135 (1988) 2669.
18. M. Dubois, G. Froyer, D. Billaud, *Synth. Met.* 97 (1998) 217.
19. J. Coetzer, *J. Power Sources* 18 (1986) 377.
20. C.H. Dustmann, J.L. Sudworth, Proceedings 11th Int. Electric Vehicle Symposium Florenz, Italy, 27-30 Sept. 1992, 1-10.
21. R.C. Galloway, S. Haslam, *J. Power Sources* 80 (1999) 164.
22. J. Prakash, L. Redey, D.R. Vissers, *J. Power Sources* 87 (2000) 195.
23. J. Badoz-Lambling, M. Bardin, C. Bernard, B. Fahys, M. Herlem, A. Thiébault, G. Robert, *J. Electrochem. Soc.* 135 (1988) 587.
24. B. Fahys, C. Bernard, G. Robert, M. Herlem, *J. Power Sources* 20 (1987) 305.
25. M. Herlem, M. Székely, E. Sutter, C. Mathieu, A.-M. Gonçalves, E. Caillot, G. Herlem, B. Fahys, *Electrochimica Acta* 46 (2001) 2967.
26. E. Peled, in «Lithium Batteries» J.P. Gabano, Editor, p. 47, Academic Press, New York (1983).
27. M. Lazzari and C.A. Vincent, chapter: «Ambient liquid electrolyte cells», in «Modern batteries – an introduction to electrochemical power sources», C.A. Vincent, F. Bonino, M. Lazzari, B. Scrosati, Editors, p. 163, Edward Arnold Publ. London (1984).
28. In «Modern Electrochemistry», J. O'M. Bockris, A.K.N. Reddy, Eds., Vol. 2, p.744, 3rd printing, Plenum/Rosetta Ed., Plenum Press, New York (1977).
29. H. Uchida, H.W. Lei, M. Hiei and M. Watanabe, *Proc. Electrochem. Soc.* 96-8 (1996) 83.
30. Γ^- and CN^- ions have a very similar adsorption behavior. Even in reduction potentials, at a smooth polycrystalline Pt electrode, CN^- adsorb strongly, as shown by spectroscopic investigation (this is not possible with Γ^- ions). See for ex. A. Tadjeddine, P. Guyot-Sionnest, *Electrochim. Acta* 36 (1991) 1849.