

Room temperature molten salt as medium for lithium battery

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Abstract

Due to the wide electrochemical window and high ionic conductivity, the 1-methyl-3-ethylimidazolium chloride (MeEtImCl) room temperature molten salt (RTMS) was investigated as the medium for lithium battery in the present work. The addition of $C_6H_5SO_2Cl$ to the RTMS was shown to improve its chemical stability and the reversibility of the lithium electrode because of the removal of $Al_2Cl_7^-$ from the melt. Electrochemical reaction which occurred at the $LiCoO_2$ was studied and the carbon current collector was found to interact with the melt. Out of the various carbon materials studied, graphite was found to be the best material. A $LiAl/LiCoO_2$ battery using RTMS as the electrolyte was assembled for battery test. Satisfactory results were obtained in preliminary cycling, showing a cell voltage of 3.45 V with better than 90% coulombic efficiency and a discharging capacity of 112 mA h/g $LiCoO_2$ at current density of 1 mA/cm². © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Room temperature molten salt; Lithium battery; Aluminium chloride; Lithium cobalt oxide; 1-Methyl-3-ethyl-imidazolium chloride; $C_6H_5SO_2Cl$

1. Introduction

The recently developed room temperature molten salt (RTMS) comprising of the 1-methyl-3-ethylimidazolium chloride (MeEtImCl) and aluminium chloride has been shown to possess desirable properties of high conductivity, non-flammability, thermal stability and chemical inertness [1,2]. The neutral molten salt ($AlCl_3/MeEtImCl = 1$) enriched by $LiAlCl_4$ exhibited wide electrochemical window of 4.5 V [3], leading to the present study of its applicability as the medium for lithium battery.

In order to provide a suitable medium for lithium battery, the RTMS medium has to be characterised, in particular, the electrokinetic characteristics of the highly reactive lithium electrodes. Several additives such as benzene, water, HCl and $SOCl_2$ had been found to lower the cathodic limit of the RTMS and improve the reversibility of the lithium electrode [4,5]. The reports of reversible co-deposition of $LiAl$ on aluminium electrode or lithium electrode [6,7] and the reversible intercalation of lithium ions into $Na_{0.7}K_{0.3}V_3O_8$ compound [8] provide additional indication that the RTMS is a feasible medium for lithium battery.

In the present work, the applicability of the RTMS as the medium for lithium battery was investigated. The effectiveness of $C_6H_5SO_2Cl$ as an additive to neutralize

excessive amount of $Al_2Cl_7^-$ was studied using cyclic voltammetry. The electrochemical characteristics of different electrode materials such as lithium, aluminium, carbon and $LiCoO_2$ were determined. A preliminary cycling test was conducted on a lithium battery in the RTMS based on the $LiAl/LiCoO_2$ system and its initial performance are reported and the results discussed in this paper.

2. Experimental

The RTMS was made up by mixing appropriate amount of MeEtImCl, aluminium chloride and $LiCl$. All chemicals were supplied from Aldrich and purified using previously reported methods [9]. The acidic binary melt ($MeEtImCl/AlCl_3 = 1/1.20$) was prepared initially prior to the addition of solid $LiCl$ to make up the slightly acidic melt. The whole process took 24 h under constant stirring and excess amount of solid $LiCl$ was filtered off to obtain the slightly acidic melt. The molar ratios of the constituents of the melt assayed by atomic absorption spectrophotometry were: $MeEtImCl/AlCl_3/LiCl = 1.00/1.20/0.15$. The additive, $C_6H_5SO_2Cl$, was added in the final step to make its concentration up to 0.05 mol/kg melt.

$LiCoO_2$ electrode was prepared by mixing $LiCoO_2$ powder with the Teflon binder and carbon powder to produce an electrode paste which was then pressed onto a

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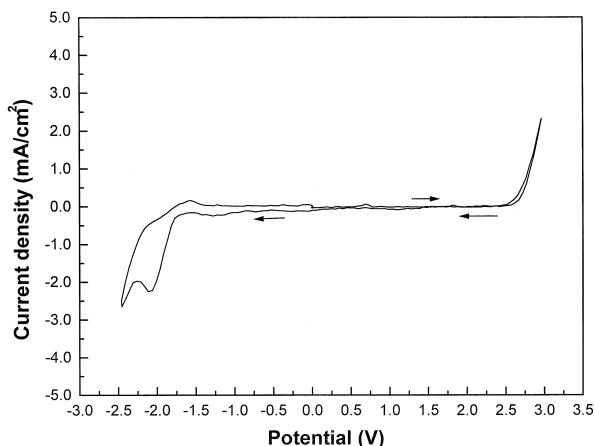


Fig. 1. The cyclic voltammogram of tungsten electrode in room temperature molten salt (MeEtImCl/AlCl₃/LiCl = 1.0/1.2/0.15). Scan rate: 20 mV/s. Reference electrode: aluminum in acidic melt (MeEtImCl/AlCl₃ = 1/1.5). Counter-electrode: aluminum. Initial potential: 0 V.

tungsten foil under pressure at 20 kg/cm². The electrode fabricated was then dried at 140°C for 10 h before use.

The electrochemical experiments were performed using the EG&G PAR Model 263 Potentiostat and Model 5210 Lock-in Amplifier. A three-electrode test cell was assembled using either tungsten, aluminium, carbon or LiCoO₂ as the working electrode, aluminum as the counter-electrode, and aluminum wire inserted into the acidic melt (molar ratio MeEtImCl/AlCl₃ = 1.0/1.5) as the reference electrode.

²⁷Al nuclear magnetic resonance (NMR) spectroscopic study was performed using the JEOL GSX-300 FT NMR spectrometer. AlCl₃-D₂O solution (10 wt.%) sealed in 5

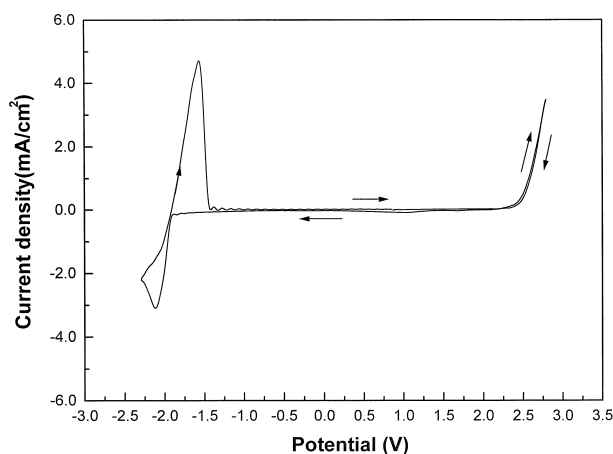


Fig. 2. The cyclic voltammogram of tungsten electrode in room temperature molten salt (MeEtImCl/AlCl₃/LiCl = 1.0/1.2/0.15) with the addition of C₆H₅SO₂Cl (0.05 mol/kg). Scan rate: 20 mV/s. Reference electrode: aluminum in acidic melt (MeEtImCl/AlCl₃ = 1/1.5). Counter-electrode: aluminum. Initial potential: 0.5 V.

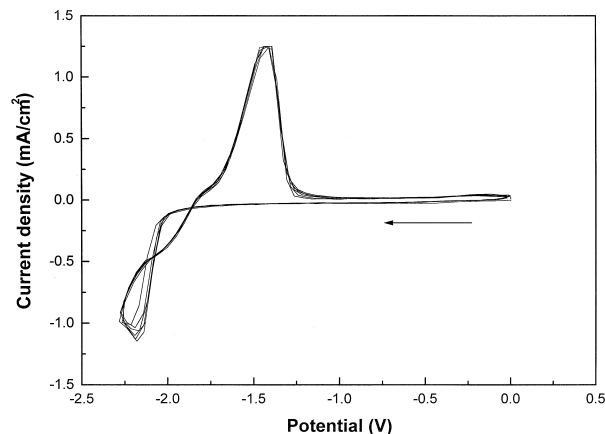


Fig. 3. The multiple cyclic voltammogram of aluminum electrode in room temperature molten salt (MeEtImCl/AlCl₃/LiCl = 1.0/1.2/0.15) with the addition of C₆H₅SO₂Cl (0.05 mol/kg). Scan rate: 20 mV/s. Reference electrode: aluminum in acidic melt (MeEtImCl/AlCl₃ = 1/1.5). Counter-electrode: aluminum. Initial potential: 0 V.

cm length capillary tubes was used as the ²⁷Al external standard for calibration.

3. Results and discussion

3.1. The MeEtImCl/AlCl₃·LiAlCl₄ melt

To investigate the electrochemical window, an inert tungsten working electrode was used to obtain the cyclic voltammogram using the RTMS. The results (Fig. 1) indicated an anodic limit at 2.5 V and a cathodic limit at -2.35 V, with an electrochemical window of 4.85 V. The anodic current is attributed to the oxidation of the AlCl₄⁻ anion and the cathodic limit, the reduction of MeEtIm⁺. The cyclic voltammogram is noted for the absence of a reverse peak, though a deposition was observed at -2.1 V. The deposition peak is attributed due to the co-deposition of Li/Al alloy and the absence of stripping due to the chemical interaction which occurred between the reactive Li/Al alloy with other chemical substances present in the melt.

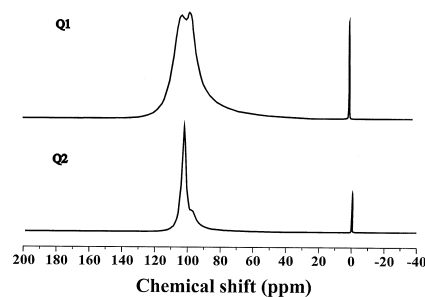


Fig. 4. The comparison of the ²⁷Al NMR spectra for Q1: RTMS alone (MeEtImCl/AlCl₃/LiCl = 1.0/1.2/0.1) and Q2: RTMS with the addition of C₆H₅SO₂Cl (10% by molar). External standard: AlCl₃ in D₂O (10%). Temperature: 25°C.

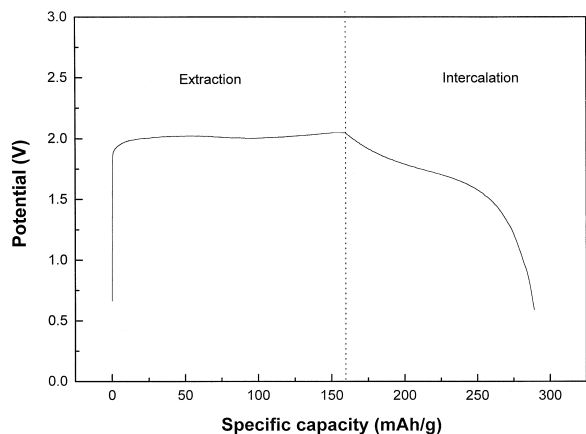
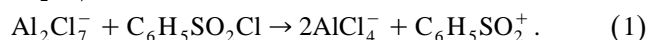


Fig. 5. The typical extraction and intercalation curves of the LiCoO_2 electrode in the RTMS with the addition of $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ (0.05 mol/kg). LiCoO_2 electrode: LiCoO_2 (85 wt.%) + graphite (10 wt.%) + Teflon (5 wt.%). RTMS: $\text{MeEtImCl}/\text{AlCl}_3/\text{LiCl} = 1.0/1.2/0.15$. Current density = $1.0 \text{ mA}/\text{cm}^2$. Reference electrode: aluminum in acidic melt ($\text{MeEtImCl}/\text{AlCl}_3 = 1/1.5$). Counter-electrode: aluminum.

In order to reduce the chemical interaction, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ was added to the melt. The following changes were observed: (1) the colour of the molten salt changed from light brown to deep brown, indicating the occurrence of chemical reaction in the molten salt; (2) no darkening of fresh lithium metal surface was observed upon its insertion into the melt, indicating that the molten salt was stabilized by the additive; and (3) a stripping peak appeared at -1.6 V in the cyclic voltammogram as given in Fig. 2. The above results show that the reversibility of the lithium electrode in the RTMS in the presence of the additive is greatly improved. Multiple cycling of the aluminium electrode gave highly repetitive voltammograms (Fig. 3), and hence, indicating the reversibility of the lithium–aluminum electrode upon electrochemical cycling in the presence of the additive.

In order to understand the chemical interaction of the $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ additive, the ^{27}Al NMR spectra for the acidic molten salt with and without the addition of $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ were recorded. Two peaks were found at chemical shift of 97 ppm and 102 ppm as shown in Fig. 4, indicating the existence of the AlCl_4^- and Al_2Cl_7^- anions in the molten salt. After the addition of $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ (10 wt.%), the peak at 97 ppm disappeared, indicating the occurrence of a

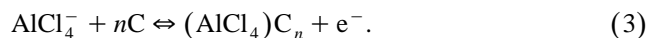
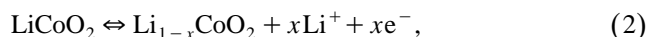
chemical reaction in the melt. The chemical reaction may involve the following reaction of the additive with the Al_2Cl_7^- anions:



In the above reaction, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ is acting as a Lewis base and its reaction with Al_2Cl_7^- anion will reduce the chemical reactivity of the melt, which is mainly governed by the reactive Al_2Cl_7^- anion. When a lithium foil was immersed in pure $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ for several days, a gray outer layer was observed. Results of chemical analysis showed that it was LiCl . The formation of the surface layer is due to the strong oxidising power of $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ which could react with the lithium electrode to produce a protective LiCl film. Formation of a passivated film at the electrode surface was further supported by the AC impedance results which gave a continued increase of the interface resistance of the lithium electrode upon cycling.

3.2. The $\text{Li}_{1-x}\text{CoO}_2$ electrode

Fig. 5 shows the extraction and intercalation curve of the $\text{Li}_{1-x}\text{CoO}_2$ electrode in the RTMS using different carbon materials as the current collector at a constant current of $1 \text{ mA}/\text{cm}^2$. Table 1 gives the variation of the extraction and intercalation capacities of the $\text{Li}_{1-x}\text{CoO}_2$ electrode upon cycling. The results indicate a much higher extraction and intercalation capacities of the electrodes in the RTMS as compared to those obtained in $1 \text{ M LiClO}_4/\text{PC}$ at the first cycle [10]. Possible electrochemical reactions are given in Eqs. (2) and (3).



The cyclic voltammogram of the graphite electrode (Fig. 6) shows poor reversible intercalation of AlCl_4^- into graphite and this accounts for the loss of capacity at the first cycle. Out of various carbon materials studied (Table 1), the more amorphous acetylene black electrode gave the lowest coulombic efficiency for both the first and the 20th cycle, whereas graphite electrode with a layer structure gave the highest coulombic efficiency for both cycles. The variation of the specific capacity upon cycling was given in Fig. 7. The results indicate that the loss of specific capacity was gradually reduced upon cycling and stable

Table 1

The variation of the extraction and intercalation capacities upon cycling of the $\text{Li}_{1-x}\text{CoO}_2$ electrode in the RTMS using different current collectors at $1 \text{ mA}/\text{cm}^2$ constant current

Cycle number	Capacity and coulombic efficiency	$\text{Li}_{1-x}\text{CoO}_2$ electrodes mixed with		
		Graphite	Petroleum coke	Acetylene black
1st	Extraction capacity (mAh/g)	240	335	450
	Intercalation capacity (mAh/g)	141	131	116
	Coulombic efficiency (%)	58.8	39.1	25.8
20th	Extraction capacity (mAh/g)	151	150	141
	Intercalation capacity (mAh/g)	138	127	113
	Coulombic efficiency (%)	91	84	80

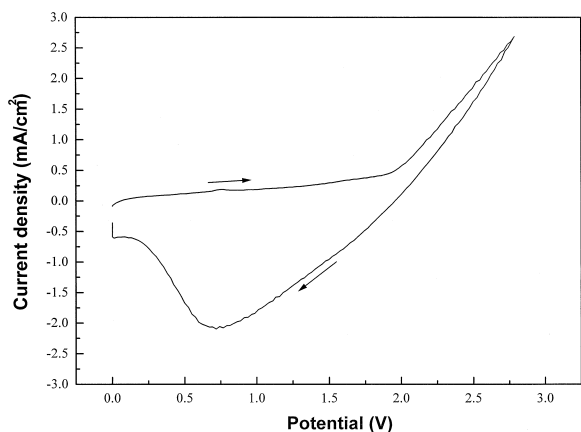


Fig. 6. The cyclic voltammogram of graphite electrode in room temperature molten salt (MeEtImCl/AlCl₃/LiCl = 1.0/1.2/0.15) with the addition of C₆H₅SO₂Cl (0.05 mol/kg). Scan rate 5 mV/s. Reference electrode: aluminum in acidic melt (MeEtImCl/AlCl₃ = 1/1.5). Counter-electrode: aluminum. Initial potential: 0 V.

extraction/intercalation curves and over 90% coulombic efficiency were obtained after the initial five cycles.

3.3. The LiAl/Li_{1-x}CoO₂ battery system

To study the cycling behaviour of the LiAl|RTMS|Li_{1-x}CoO₂ battery system, an electrochemical cell was assembled in the discharged state using pure aluminium and LiCoO₂ electrode (LiCoO₂: 85 wt.%, graphite: 10 wt.%, Teflon: 5 wt.%) in the RTMS. Upon initial charging for a few cycles at 1 mA/cm², the positive electrode (Li_{1-x}CoO₂) and the negative electrode (LiAl) were formed. The cycling life and specific capacity of the battery were then determined at 1.0 mA/cm² at a charging

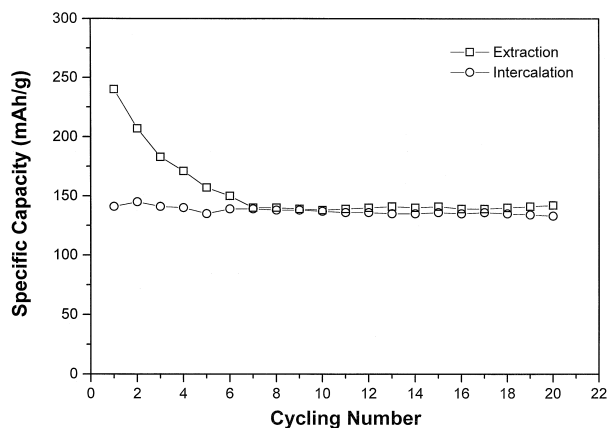


Fig. 7. The variation of the extraction and intercalation capacities of the LiCoO₂ electrode upon cycling in the RTMS with the addition of C₆H₅SO₂Cl (0.05 mol/kg). LiCoO₂ electrode: LiCoO₂ (85 wt.%) + graphite (10 wt.%) + Teflon (5 wt.%). RTMS: MeEtImCl/AlCl₃/LiCl = 1.0/1.2/0.15. Current density = 1.0 mA/cm². Reference electrode: aluminum in acidic melt (MeEtImCl/AlCl₃ = 1/1.5). Counter-electrode: aluminum.

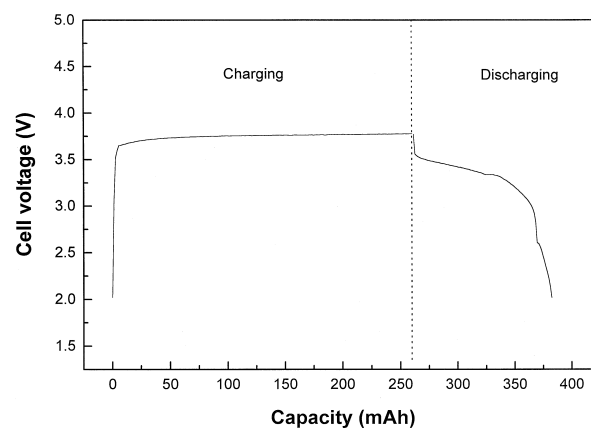


Fig. 8. The variation of the cell voltage of the LiAl/LiCoO₂ battery using the RTMS as the electrolyte media with the addition of C₆H₅SO₂Cl (0.05 mol/kg) at first cycle. Positive electrode: LiCoO₂ (85 wt.%) + graphite (10 wt.%) + Teflon (5 wt.%). RTMS: MeEtImCl/AlCl₃/LiCl = 1.0/1.2/0.15. Current density = 1.0 mA/cm².

limit of 4.2 V and a discharging limit of 2.9 V (Fig. 8). The average discharging voltage was 3.45 V. When only active Li_{1-x}CoO₂ material was used for calculation, the maximum specific discharging capacity was 112 mA h/g. Results showing the variation of the battery voltage upon cycling was shown in Fig. 9. Lower coulombic efficiencies were found at the initial few cycles. As similar observations were observed in the basic electrochemical study using Li_{1-x}CoO₂ as the working electrode, the results indicate that Li_{1-x}CoO₂ is the limiting electrode in the overall battery system. Moreover, the coulombic efficiencies obtained in the battery system are slightly lower than the Li_{1-x}CoO₂ electrode alone, indicating the occurrence of other electrochemical reactions leading to the reduction in the coulombic efficiency, though their effects are much

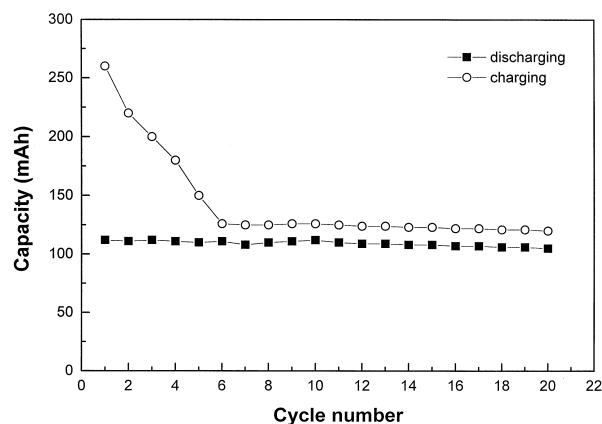


Fig. 9. The variation of the charging and discharging capacities of the LiAl/LiCoO₂ battery upon cycling using the RTMS as the electrolyte medium with the addition of C₆H₅SO₂Cl (0.05 mol/kg). Positive electrode: LiCoO₂ (85 wt.%) + graphite (10 wt.%) + Teflon (5 wt.%). RTMS: MeEtImCl/AlCl₃/LiCl = 1.0/1.2/0.15. Current density = 1.0 mA/cm².

less as compared to the $\text{Li}_{1-x}\text{CoO}_2$ electrode. Current work is undertaken to investigate the effect of long-term cycling and high current charging/discharging using the RTMS battery system.

4. Conclusions

To investigate the applicability of the 1-methyl-3-ethyl-imidazolium chloride/ $\text{AlCl}_3 \cdot \text{LiAlCl}_4$ RTMS system for lithium ion battery use, electrochemical study of the melt, with and without the addition of $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$, was performed. The stability of the neutral molten salt and the reversibility of the lithium electrode in the melt were shown to be greatly improved by the addition of $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$. The improvement was attributed to the removal of Al_2Cl_7^- in the melt. The electrochemical reaction of the $\text{Li}_{1-x}\text{CoO}_2$ electrode was studied and the carbon current collector was found to interact with the melt. Out of the various carbon materials studied, graphite was found to give the best performance. A $\text{LiAl}/\text{Li}_{1-x}\text{CoO}_2$ battery using RTMS as the electrolyte was assembled for cycling test. Satisfactory results were obtained in the preliminary cycling, showing an average cell voltage of 3.45 V with better than 90% coulombic efficiency and a discharging capacity of 112 mAh/g at current density of 1 mA/cm². Current work is undertaken to investigate the effect of

long-term cycling and high current charging/discharging on the RTMS battery system.

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