Journal of Electroanalytical Chemistry 757 (2015) 167–175

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jeac

Ionic liquid electrolytes for aluminium secondary battery: Influence of organic solvents

Shuang Xia, Xiao-Min Zhang, Kuan Huang, Yong-Le Chen, You-Ting Wu *

Separation Engineering Research Center, Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China

ARTICLE INFO

Article history:
Received 6 May 2015
Received in revised form 9 September 2015
Accepted 15 September 2015
Available online 18 September 2015

Keywords:
Aluminium secondary battery
Ionic liquid
Sulfur–carbon electrode
Electrochemistry

ABSTRACT

Physical and electrochemical characteristics of aluminium secondary battery systems based on aluminium anodes, sulfur–carbon cathodes and ionic liquid electrolytes were investigated. Aluminium chloride ($AlCl_3$)/triethylamine hydrochloride (Et_3NHCl) ionic liquids were used as the electrolytes. Toluene, benzene, dichloromethane (DCM), and 1,2-dichlorethane (DCE) were tested as the additives to modify the performance of ionic liquid electrolytes. DCM and DCE were found to be the better choices, with 0.2 as the optimized volume ratio of organic solvent to ionic liquid. The additives have functions of reducing the viscosities and elevating the conductivities of ionic liquid electrolytes, while having little influence on the thermal stability of battery system in normal working temperature range. To assess the electrochemical properties of the electrolytes, galvanostatic charge/discharge studies were performed at the cell voltage of 2.4 V to 0.6 V at a constant current discharge of 15 mA/g. The cell exhibits well-defined discharge voltage plateaus near 1.8 V. A discharging capacity of 113.64 mAh/g at the first cycle is obtained for the cell based on DCM-ionic liquid electrolyte, in comparison with 85.23 mAh/g for the cell based on pure IL. The discharging capacity has the highest value of 131.67 mAh/g, and remains 104.69 mAh/g after 40 cycles. This study indicates that the performance of aluminium secondary battery can be greatly improved by adding a small volume of organic additives to the ionic liquid electrolytes.

1. Introduction

Nowadays, Li-ion battery has dominated the rechargeable battery market. A great amount of research keeps improving its performance in every aspect: the life cycle, working voltage, power and energy density, safety and cost, thereby supporting parallel advances in mobile technology and transportation. However, the concerns regarding the high cost and the limited lithium reserves in the earth's crust have driven the researchers to search more sustainable alternative energy storage solutions [1–6]. As the most abundant metallic element in the earth's crust, aluminium comes to scientists' sight. The volumetric charge-storage capacity of aluminium metal is 8.0 Ah/cm^3, which is about four times the capacity of lithium (2.062 Ah/cm^3). Aluminium is also competitive in terms of gravimetric capacity (3.0 Ah/g versus lithium's 3.9 Ah/g or magnesium's 2.2 Ah/g). The higher production and less expensive raw material than lithium also make aluminium a promising material for batteries.

Rechargeable aluminium batteries based on high temperature molten salt electrolytes have been the subject of extensive research [7]. However, the high working temperature, high cost and difficulty in maintaining limit its development. Recently, researchers begin to use ambient temperature ionic liquids (ILs) as the electrolytes of rechargeable aluminium batteries. The chloroaluminate ILs (CILs) known as "the first generation" ILs, have been widely applied in aluminium electrodeposition [8–14]. Due to the relatively high conductivity, wide electrochemical window, and tunable acidity, the CILs can also be of great value to the electrolyte of battery. In addition, since both aluminium metal and CIL electrolytes are nonflammable, a battery based on these components may have significant safety advantages over conventional lithium- and sodium-based batteries. Furthermore, the conductivities of imidazolium-based CILs are comparable with those of lithium-ion battery electrolytes [15–17]. One early demonstration of CIL used as the secondary battery electrolyte was the mixtures of 1,4-dimethyl-l,2,4-triazolium chloride (DMTC) and aluminium chloride [18], in which DMTC-$AlCl_3$ electrolyte was proved to be acceptable for battery performance.

More recently, studies have been focused on the "aluminium-ion" battery. Jayaprakash et al. demonstrated a rechargeable aluminium battery prepared by combining a room temperature ionic liquid electrolyte with a vanadium pentoxide (V_2O_5) nanowire composite cathode, but the battery suffered from an unexpectedly low voltage and energy density, and failed after 20 cycles [19]. The role of V_2O_5 in the composite cathode of this electrochemical system was studied [20], showing that electrochemical activity and apparent capacity at the cathode of the V_2O_5/Al cell were wholly attributed to a reaction between the CIL and the stainless steel current collector. VO_2 pasted on stainless steel was then tried as the cathode material [21], which also suffered from a low

---

* Corresponding author.
E-mail address: ytwu@nju.edu.cn (Y.-T. Wu).

http://dx.doi.org/10.1016/j.jelechem.2015.09.022
1572-6657/

voltage. MnO_2 [22], fluorinated graphite [23] were also used as Al(III)-insertion hosts in CIL electrolytes, but there was no evidence of an aluminium-intercalated phase. Subsequently, conducting polymers were used as the positive electrode, to realize excellent stability and efficiency [24]. The energy density of the polythiophene-CIL-aluminium cell was estimated as 44 Wh/kg, and that of the polypyrrole-CIL-aluminium cell was 46 Wh/kg. However, significantly sloping voltage profiles for charge and discharge were observed, implying that the amount of practical voltage obtained from the battery for a full discharge was limited. So due to problems such as low cell discharge voltage, capacitive behavior without discharge voltage plateaus and insufficient cycle life, these Al batteries failed to compete with other battery systems. Then a breakthrough was made by M.C. Lin et al. [25], using a three-dimensional graphitic-foam cathode. The cell exhibited discharge voltage plateaus near 2 V and a coulombic efficiency of approximately 98%. The cathode was found to enable fast anion diffusion and intercalation, affording charging times of around one minute with a current density of 4000 mA/g and to withstand more than 7500 cycles without capacity decay. The specific capacity is about 70 mAh/g, which needs to be improved.

Different from the Al-ion battery, here we propose a rechargeable aluminium battery that uses sulfur–carbon cathodes and aluminium anodes. So similar to the lithium–sulfur battery, our battery can be called aluminium–sulfur battery to some extent, which is reported for the first time. We also pay great attention to the electrolyte of aluminium secondary battery, due to the fact that the capacity is highly dependant on the electrolyte. As to improving the performance of aluminium battery by modifying the CIL electrolytes, few efforts have been made. CILs consisting of imidazolium salts and aluminium chloride, such as $AlCl_3$/EmimCl (l-ethyl-3-methylimidazolium chloride) [9,11,12], $AlCl_3$/TMPAC (trimethylphenylammonium chloride) [10,29] and $AlCl_3$/EmimBr (1-ethyl-3-methylimidazolium bromide) [13], have been studied in the electrodeposition. $AlCl_3$/EmimBr has the highest conductivity, but the narrow electrochemical potential window limits its application as the electrolyte. EmimCl and BmimCl are good choices, but from the perspective of fundamental research and industrial application, we prefer Et_3NHCl, because it is much cheaper than the imidazolium salts. $AlCl_3/Et_3NHCl$ has been reported in literature just for once [14], in which only nucleation process and aluminium electrodeposition on Al electrode were concerned. In this work, a comprehensive and systematic study was made on $AlCl_3/Et_3NHCl$ to explore its possible use as the electrolyte of aluminium battery. Benzene, toluene, dichloromethane (DCM), and 1,2-dichlorethane (DCE) were chosen as additives to the ionic liquid to improve the performance of the electrolytes, and the effects of additives on the electrolytes were also investigated.

2. Experimental section

2.1. Materials

All of the chemicals used in this work were purchased commercially from Aladdin Chemical Reagent Co. Ltd., Haycarb PLC Co. and Acros Organics. These reagents of analytic grade were anhydrous aluminium chloride (mass fraction ≥ 99%), Et_3NHCl (≥99%), sublimed sulfur (≥99.95%, powder), activated carbon (100%), 1,2-dichlorethane (AR grade, ≥99.5%), dichloromethane (AR grade, ≥99.5%), benzene (AR grade, ≥99.5%), and toluene (AR grade, ≥99.5%). The latter four reagents were organic solvents that were further purified by distillation and stored in closed bottles in a nitrogen filled glove box (Universal, Mikrouna Co., China). The water and oxygen contents in the glove box were below 0.1 ppm.

2.2. Synthesis of the electrolytes

$Et_3NHCl/AlCl_3$ ionic liquids with different apparent mole fractions, x, of $AlCl_3$ ($x = 0.5833$, 0.6154, 0.6429 and 0.6667) were synthesized by mixing precisely Et_3NHCl with anhydrous $AlCl_3$ at the molar ratios of 1:1.4, 1:1.6, 1:1.8, and 1:2.0, respectively. A light white smoke was observed in the mixing process due to the highly exothermic reaction occurring between $AlCl_3$ and Et_3NHCl, and care should be taken to control the reaction rate and avoid the decomposition of the ionic liquids. A faint yellowish liquid was formed after mixing. In our studies, the ionic liquids as formed above were used without further purification, so that the electrodeposition of aluminium can be investigated in a condition similar to the case of a real cell. The organic solvents were added to the CILs, with the volume ratios (n) of 0.2, 0.4, 0.6, 0.8 and 1.0. The colors of the electrolyte solutions were usually deepen due to the additives.

2.3. Characterization of the electrolytes

The electrical conductivities were obtained through a conductivity meter (DDS-307, Leici Co., China) equipped with two conductivity probes (DJS-1C, DJS-10C) in the nitrogen-filled glovebox. Densities were determined using an Anton Paar DMA 5000 type automatic densimeter with a precision of 0.000001 g/cm^3, which was calibrated using distilled water. Viscosities were measured on a HAAKE Rheostress 600 viscometer with an uncertainty of $\pm 1\%$ in relation to the full scale. The melting temperature and decomposition temperature were determined from the TG (PerkinElmer, Pyris 1 TGA) from 25 to 600 °C at a scan rate of 10 °C/min under N_2 atmosphere.

All cyclic voltammetry measurements were performed at room temperature in about 5 mL static ionic liquid, using a conventional three-electrode cell in an electrochemical workstation LK2010 (Lanlike Chemical High-Tech Co. Ltd.). The conventional cell consisted of a working electrode, a counter electrode and a reference electrode. The working electrode sealed inside a Teflon tubing of 2–3 cm length was fixed into a banana socket. The electrode surface was exposed from the end of the Teflon. The other end of the electrode was connected by a copper spring with a copper or tungsten rod plugged in the banana socket. Tungsten wire ($d = 4$ mm) and aluminium rod ($d = 4$ mm) were used as the materials of the working electrode. Pt sheet was used as the counter electrode. The reference electrode was an aluminium wire contained in a separate compartment, which was brought close to the working electrode via a Luggin probe to minimize the IR potential drop between the working electrode and the sensing point. The tungsten electrode was polished successively to a mirror-like finish with increasingly finer grades of emery paper. A final polishing was done using an aqueous slurry of 0.05 μm alumina. After polishing, the electrode was rinsed with distilled water and then acetone prior to use. The aluminium electrode was chemically polished by immersing into a solution of H_2SO_4 (98 wt.%): H_3PO_4 (85 wt.%): HNO_3 (52.5 wt.%) (25:70:5 by volume) for 25 min.

The electrochemical measurements of batteries were performed by using BT2000 (Arbin Instruments Co. Ltd., China). The electrochemical cell for charge–discharge studies was assembled by using Al foils (30 cm^2) as anode and sulfur–carbon composites as cathode. 70 parts by weight (pbw) of sublimed sulfur and 30 pbw of activated carbon were mixed in a ball mill for 10 h at 150 r/min, and heated for 24 h at 150 °C and further at 300 °C for 2 h. After these steps, the sulfur–carbon composites were prepared. To prepare the cathode, 85 pbw of sulfur–carbon composites, 5 pbw of acetylene black and 10 pbw of PTFE were mixed into a slurry and the slurry was cast on a foam nickel (30 cm^2) and dried at 80 °C under vacuum.

3. Results and discussion

3.1. Physical properties of electrolytes

3.1.1. Physical properties of $AlCl_3/Et_3NHCl$

Table 1 shows the conductivities, densities, viscosities and molar conductivities of $AlCl_3/Et_3NHCl$ at 298.15 K. It is well-known that the predominant presence of anions can be expressed as $AlCl_4^-$ and $Al_2Cl_7^-$, respectively. With the increase of mole fraction of $AlCl_3$, the molar concentration of $Al_2Cl_7^-$ increases, which causes the density to increase due