Graphene Nanoplatelet-Polysulfone Composite Cathodes for High-Power Aluminum Rechargeable Batteries

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ABSTRACT

Low-cost graphene nanoplatelet-polysulfone composite cathodes for a rechargeable aluminum battery with a Lewis acidic AlCl₃–1-ethyl-3-methylimidazolioum chloride ([C₂mim]Cl) ionic liquid are prepared by a standard slurry-coating method for the composite electrode, and conductive additives such as acetylene black (AB), ketjen black (KB), and vapor grown carbon fiber (VGCF) are explored in order to improve the cathode performance. All the cathodes show reversible electrode reactions related to the intercalation reaction of [AlCl₄]⁻ into the graphene nanoplatelets. The cathodes achieve a discharge capacity of ca. 70–80 mAh g⁻¹ at 1000 mA g⁻¹. However, the rate capability and the capacity retention rate strongly depend on the conductive additive species. The best cathode performance is obtained when the additive is an equal mixture of VGCF and KB. The specific capacity is ca. 55 mAh g⁻¹ at 10000 mA g⁻¹. The retention rate based on the capacity observed at 1000 mA g⁻¹ exceeds 65%. A Ragone plot constructed from the data shown in this article suggests that an Al rechargeable battery with a VGCF-KB added graphene nanoplatelet-polysulfone composite cathode has great potential as a future high-power density rechargeable battery.

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Keywords : Aluminum, Rechargeable Battery, Cathode, Conductive Additive

1. Introduction

One of the key technologies to support a comfortable lifestyle is rechargeable batteries. Lithium-ion batteries (LiBs) are widely used due to their remarkable energy density and cyclability. However, to meet the growing demand for LiBs, next-generation battery systems have been developed where the electrode reactions are based on new concepts. From a practical point of view, battery components based on commonly used and less expensive elements are preferable. Several potential battery systems, including Li–sulfur,1 Li–air,2 sodium ion,3 and multivalent metal rechargeable batteries,4–7 are receiving increased attention.

A multivalent metal rechargeable battery is different in that the number of electrons involved in the electrode reaction varies between two or three. Aluminum and magnesium are often used as the multivalent metals. These metals show very high theoretical volumetric capacities, 8046 mAh cm⁻³ for Al and 3833 mAh cm⁻³ for Mg, over Li metal (2062 mAh cm⁻³). Unfortunately, it is not easy to use them thoughtfully as anodes because, in most cases, they do not achieve a sufficient Coulombic efficiency in conventional electrolytes.4

In the field of Al electroplating, Al electrodeposition/striping occurs in halolaminic room-temperature ionic liquids (RTILs) with a high Coulombic efficiency according to the following electrochemical reaction:

\[ \text{[AlCl₃]}^{-} + 3e^{-} \rightarrow \text{Al} + 7 \text{[AlX₄]}^{-} \quad (\text{X: Cl or Br}) \]  

(1)

This electrochemical reaction is observed only in Lewis acidic halolaminic molten salts and RTILs with the [AlₓX₄₋]⁻ anions (X: Cl or Br). Numerous papers on pure Al and its alloy electroplating have been reported.8 Most studies were carried out in a Lewis acidic AlCl₃–1-ethyl-3-methylimidazolioum chloride ([AlCl₄–][C₂mim]Cl) RTIL [AlCl₃ molar fraction > 50 mol%], which shows flame retardation, negligible vapor pressure, relatively high ionic conductivity, and electrochemical stability.9,10 Several Al rechargeable battery systems were proposed more than two decades ago, although they did not attract much attention at that time. In 2014, we reported an energy storage device consisting of an Al anode, an activated carbon fiber cloth cathode, and a Lewis acidic AlBr₃–1-ethyl-3-methylimidazolioum bromide (AlBr₃–[C₂mim]Br) RTIL (AlBr₃ molar fraction > 50 mol%).11 Recently, Dai and coworkers demonstrated Al rechargeable batteries with a pyrolytic graphite foam cathode and a Lewis acidic chloroaluminate RTIL.12 Other carbon material such as carbon paper,13 few-layer graphene film,14 3D graphene nanoarchitected,15 and graphene-coated carbon fiber cloth16 have also been recognized as promising cathodes. Taking advantages of the well-developed slurry-coating protocol, we very recently demonstrated that Al-based rechargeable batteries can be fabricated using polymer composite cathodes with commercially available and inexpensive graphene nanoplatelets as the cathode active material.17 Interestingly, these composite electrodes show favorable cathode performances comparable to those of sophisti-
catedly fabricated ones.12,14,15

In this article, we attempt to improve the cathode characteristics of the aforementioned graphene nanoplatelet composite electrode for Al rechargeable batteries by adding conductive additives such as acetylene black (AB), ketjen black (KB), and vapor grown carbon fiber (VGCF). The electrochemical behavior and cathode performance of the prepared electrodes are examined in a Lewis acidic 60.0–40.0 mol% AlCl₃–[C₂mim]Cl RTIL. Additionally, the power density is discussed by a Ragone plot for a composite cathode containing both KB and VGCF additives, which shows the best cathode performance.
2. Experimental

AlCl$_3$–[C$_2$mim]Cl RTIL (60.0–40.0 mol%) was prepared using the procedure reported by Hussey et al.$^9$ Anhydrous AlCl$_3$ (ultra-high purity, specially manufactured grade, Nippon Light Metal Company) was used without further purification. After the purification process of [C$_2$mim]Cl (Merck), AlCl$_3$ was gradually added to [C$_2$mim]+ cations because this simple RTIL synthesis is severely exothermic. The crude Lewis acidic RTIL (ca. 50 mL) was purified by a constant-current electrolysis between the Al cathode and the anode at $\approx 10$ mA for 72 hours under agitation. This procedure gave clear and colorless AlCl$_3$–[C$_2$mim]Cl RTIL. All preparations and electrochemical experiments were conducted in an argon gas-filled glove box (Vacuum Atmospheres Co., NEXUS II system) with O$_2$ and H$_2$O contents $<$1 ppm.

A graphene nanoplatelet composite cathode without conductive additives, which was composed of 80 wt% graphene nanoplatelets (Strem Chemicals, width: 5 µm; thickness: 6–8 nm) and 20 wt% polysulfone (Aldrich), was prepared by the following procedure. An adequate amount of chlorobenzene (Guaranteed Reagent, Wako) was added to the graphene nanoplatelets and thoroughly blended by ball milling. The homogenous slurry was coated onto a molybdenum (Mo) plate current collector and dried under vacuum at 373 K for 12 hours.

In the same manner, graphene nanoplatelet composite cathodes with conductive additives were produced, but the composition ratio was 70 wt% graphene nanoplatelets, 20 wt% polysulfone, and 10 wt% conductive additives. The employed conductive additives were AB, KB, VGCF, KB-VGCF mixture (5 wt%:5 wt%). These preparation processes are schematically depicted in Scheme 1.

Electrochemical experiments were conducted in a three-electrode cell connected with an IVIUM Technologies CompactStat potentiostat/galvanostat or a Hokuto Denko HJ-1001SD battery cycling system. The graphene nanoplatelet composite cathodes and a coil of 1.0-mm-diameter Al wire (Nilaco, 99.999%) were used as the working electrodes and the counter electrode, respectively. A Mo plate (Nilaco, 99.8%, 1 x 1 cm) was also employed as the working electrode to verify the electrochemical stability of the Mo current collector. The reference electrode (Al(III)/Al) was constructed by placing a 1.0-mm-diameter Al wire into a 12-mm-diameter Pyrex tube terminated with a porous G-4 glass frit (Vidrex). An electrolyte for the reference electrode was a 60.0–40.0 mol% AlCl$_3$–[C$_2$mim]Cl RTIL. The aluminum electrodes were cleaned with a mixture of concentrated H$_2$SO$_4$, HNO$_3$, and H$_3$PO$_4$, rinsed with distilled water, and dried under a vacuum before use. Prior to the charge-discharge experiments, a pretreatment process was conducted at 1000 mA g$^{-1}$ for 10 cycles to stabilize the electrode. All the experiments were conducted in the argon gas-filled glove box described above. The specific capacity and current density were calculated using the weight of graphene nanoplatelet.

3. Results and Discussion

In this study, five types of graphene-polysulfone binder composite electrodes (with or without conductive additives) were prepared. Figure 1 shows the cyclic voltammograms recorded at those electrodes in a 60.0–40.0 mol% AlCl$_3$–[C$_2$mim]Cl RTIL. For comparison, a voltammogram at a Mo current collector that shows no electrochemical anodic dissolution and has a high Cl$_2$ gas...
Figure 2. Chronopotentiograms recorded at graphene nanoplatelet composite electrodes in a 60–40 mol% AlCl3-[C2mim]Cl. The electrodes were (black, —) the original composite electrode without a conductive additive and with (red, —) AB, (blue, —) KB, (green, —) VGCF, and (orange, —) VGCF (5 wt%) + KB (5 wt%). The temperature was room temperature. The cut off potentials were 2.4 and 0.8 V vs. Al(III)/Al. The applied current density was 2000 mA g⁻¹.

Figure 3. (a) Specific capacity for (filled triangle) charge and (open circle) discharge, (b) capacity retention rate for discharge process, and (c) Coulombic efficiency estimated from the charge-discharge tests conducted at graphene nanoplatelet composite cathodes in a 60–40 mol% AlCl3-[C2mim]Cl. The electrodes were (black) the original composite electrode without a conductive additive and with (red) AB, (blue) KB, (green) VGCF, and (orange) VGCF (5 wt%) + KB (5 wt%). The cut off potential were 2.4 and 0.8 V vs. Al(III)/Al. The applied charge-discharge current densities were 1000 to 10000 mA g⁻¹.

The corresponding Coulombic efficiency data are given in Fig. 3c. As expected from Fig. 2, the specific charge and discharge capacities for the composite cathodes without conductive additives and with AB are inferior to the other three cathodes. Adding KB and VGCF to the composite electrode obviously leads to a higher specific capacity. Their discharge capacities are ca. 80 mAh g⁻¹ at a current density of 1000 mA g⁻¹. VGCF-added cathode shows a better rate capability and capacity retention rate because the wire-like VGCF readily forms a well-connected conducting network with graphene nanoplatelets. However, the Coulombic efficiency of the composite electrode with VGCF is lower than those with no additive, AB, and KB. Currently we do not have scientific evidence to explain this behavior, but Cl₂ generation by reaction (3) may easily proceed on the VGCF-added cathode because it is mostly covered with a physicochemically inert basal plane onto which Cl₂ is difficult to adsorb. To improve the Coulombic efficiency, both VGCF (5 wt%) and KB (5 wt%), which show favorable specific capacities and Coulombic efficiencies, were added to the composite
carbon additives and electrode characteristics given in this study should contribute to the development of high-performance Al rechargeable batteries.

Acknowledgments

This research was partially supported by JSPS KAKENHI Grant Numbers JP15H03591, JP15K13287, JP15H02202, and JP16K14539, and by the Advanced Low Carbon Technology Research and Development Program (ALCA) for Specially Promoted Research for Innovative Next Generation Batteries (SPRING), Japan Science and Technology Agency (JST). Anhydrous AlCl3 was provided by Nippon Light Metal Company.

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