Construction of aluminum rechargeable batteries and investigation of their positive electrode materials Masanobu Chiku, Hiroki Takeda, Takeshi Kunisawa, Eiji Higuchi and Hiroshi Inoue Department of Applied Chemistry, Graduated School of Engineering, Osaka Prefecture University Sakai, Osaka 599-8531, Japan

Introduction

Multivalent cation like Mg is considered as promising candidate of negative electrode material for post Li-ion batteries because Mg becomes divalent cation and shows high energy density about 3837 mAh cm⁻³. So many researchers are investigating about the Mg rechargeable batteries.

On the other hands, Al becomes trivalent cation and shows highest energy density about 8043 mAh cm⁻³, it is 4 times larger than Li metal. Jayaprakash et al. constructed Al rechargeable batteries using Al metal as negative electrode, the ionic liquid, 1-ethyl-3methylimidazolium chloride, with AlCl₃ as electrolyte and V₂O₅ nano wire as positive electrode material¹⁾. However, cyclic performance was not enough and ionic liquid is generally expensive, so new positive electrode materials and the electrolyte using inexpensive organic solvent is necessary to realize commercial Al rechargeable battery.

In this work, we constructed Al rechargeable battery using amorphous V_2O_5 positive electrode materials and organic liquid electrolyte. Legrand et al. suggested a mixture of aluminum chloride and dipropylsulfone (DPSO₂) is applicable to aluminum plating electrolyte and its melting point is 30 °C ²⁾. The same sort of electrolyte is also investigated by Toshiba co.,³⁾. We used the mixture of AlCl₃, DPSO₂ and toluene as electrolyte and we constructed Al rechargeable battery using amorphous V₂O₅ positive electrode materials.

Experimental

All electrochemical measurements were examined with coin type configuration glass cell. We employed a mixture of aluminum chloride, dipropylsulfone and toluene with the mass ratio at 1:10:5 as electrolyte for aluminum secondary battery. Aluminum plate with diameter of 10 mm was used as counter and reference electrodes for all experiments. A glass fiber filter was used as separator.

 V_2O_5 positive electrode was prepared as follow: Vanadium metal powder was dissolved into 30 wt. % hydrogen peroxide solution in ice bath and ketjen black (KB) was added. The solution was dried and residue was heated at 120 °C for 10 hours. V_2O_5 active material was pelletized into 13 mm diameter with polytetrafluoroethylene as binding agent.

Results and discussions

Figure 1a shows the CVs of Mo electrode in the $DPSO_2 + AlCl_3 + toluene$ solutions. Metallic Al was deposited onto the Mo electrode during electrochemical reduction and dissolved during electrochemical oxidation. Reversible deposition/dissolution process was observed and it suggests that our electrolyte can be applied to Al rechargeable battery.

Figure 1b shows the CVs of V_2O_5 positive electrode. Broad oxidation and reduction peaks were observed. V_2O_5 is layer compounds and Al^{3+} ion will be intercalated during discharge process and deintercalated during charging process. V_2O_5 positive electrode will work with the process as indicated as below;

$$V_2O_5 + xAl^{3+} + 3xe^{-} \rightleftharpoons Al_xV_2O_5$$
(1)

If x = 1, theoretical discharge capacity will be 442 mAh g⁻¹. Al³⁺ ion is trivalent ion and will strongly adsorb to oxygen atom in V₂O₅, so charge/discharge cycle will be inhibited. Our V₂O₅ positive electrode material showed amorphous structure from X-ray diffraction measurements. Amorphous V₂O₅ shows longer lattice distance than crystalline V₂O₅ and it seems to be favorable to increase the performance of Al ion intercalation/deintercalation cycle. Figure 2 shows the charge/discharge curbs of an Al rechargeable battery. For the 1st cycle, discharge capacity was over 400 mAh g⁻¹. After the 2nd cycle, discharge capacity became about 100 mAh g⁻¹ at 10th cycle.

Reference

- 1. N. Jayaprakash, S. K. Das and L. A. Archer, *Chem. Commun.*, **47**, 12610 (2011)
- L. Legrand, M. Heintz, A. Tranchant and R. Messina, *Electrochim. Acta*, 40, 1711 (1995)
- 3. U.S. Patent 2003/059684 A1

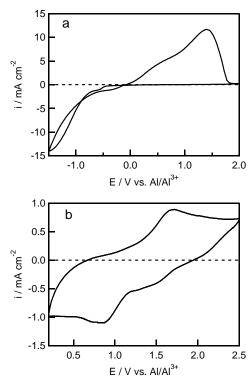


Figure 1 CVs of (a) Mo and (b) V_2O_5 electrode with DPSO₂ and toluene electrolyte.

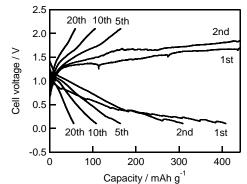


Figure 2 Charging and discharging curves of aluminum secondary battery.