多価金属負極アニオン電池開発の現状

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The Present Situation of Multivalent Metal Anode Anion Secondary Battery Development

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The expectation from society towards secondary battery is increasing more and more, recent years, the development race is highly competitive. Most are dedicated to the development of next-generation high-performance secondary battery. However, a different type of secondary battery, which has a battery performance comparable to current Li-ion battery and consists of only common elements, is also an important research target. In this context, we are working on the application of ionic liquids (ILs) obtained by mixing commonly used metal chlorides and organic chloride salts to battery electrolytes. These ILs are composed of organic cations and metal chloride complex anions, and the metal deposition/stripping reactions proceed reversibly at the cathodic limit potential. For example, as to Al, a mixture of $AlCl_3$ and an organic salt such as 1-ethyl-3-methylimidazolium chloride ([C_2mim]Cl) is usually employed as an organic IL electrolyte. In the composition region where the molar fraction of $AlCl_3$ exceeds 50 mol%, complex anion species ($[Al_2Cl_7]^-$) involved in Al deposition/stripping reactions are formed (Fig. 1), and the electrochemical reaction (equation (1)) proceeds with a coulombic efficiency close to 100 %.[1)]

$$4[Al_2Cl_7]^- + 3e^- \rightleftharpoons Al + 7[AlCl_4]^- \qquad (1)$$

Similar results have been often obtained with ILs using other metal chloride salts,[2)] but considering the merits of metal anode, attractive targets are Al and Zn with low costs and large theoretical capacities. When $AlCl_3$–[C_2mim]Cl or $ZnCl_2$–[C_2mim]Cl are selected as organic IL electrolytes, we can use the multivalent metal anode reactions of Al and Zn without difficulty. Now, finding cathodic reactions that can work in the IL electrolytes is the main subject in this research field.[3-7)] Since the ion species involved in the electrode reaction are only complex anions, these battery systems are often classified as multivalent metal anode anion batteries. In this presentation, I will introduce the present situation of R&D on inexpensive multivalent metal (Al and Zn) anode anion batteries.

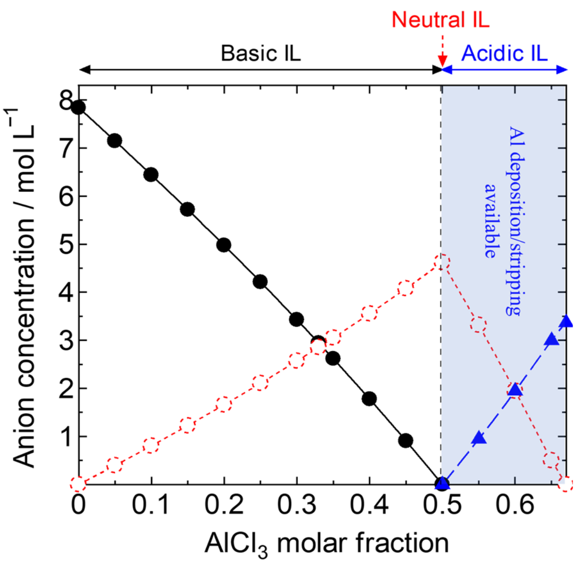

Fig. 1. Concentrations for anionic species (●: Cl^-, ○: $[AlCl_4]^-$, ▲: $[Al_2Cl_7]^-$) in the $AlCl_3$–[C_2mim]Cl ionic liquid at different $AlCl_3$ molar fractions.

Keywords: Multivalent Metal Anode; Aluminum; Zinc; Ionic Liquid; Secondary Battery

二次電池に対する社会からの期待は増大する一方であり、開発競争は年々激しさを増している。その多くは、次世代を担う超高性能二次電池に関するものであるが、現行の Li イオン二次電池に迫る性能を有する汎用元素のみで構成される二次電池の開発も重要な研究課題である。このような背景から、我々は汎用金属の塩化物塩と有機塩化物塩を混合することで得られるイオン液体の電池電解液への適用に取り組んでいる。このイオン液体は有機カチオンと金属塩化物錯アニオンから構成され、カソード限界電位において、金属の析出・溶解反応が可逆的に進行する。例えば、Al の場合、電解液には、$AlCl_3$ と 1-エチル-3-メチルイミダゾリウムクロライド（1-ethyl-3-methylimidazolium chloride ([C_2mim]Cl)）などの有機塩を混合して得られる有機イオン液体を用いることが一般的である。$AlCl_3$ のモル分率が 50 mol%を超える組成域には、Al の析出・溶解反応に利用可能な錯アニオン種（$[Al_2Cl_7]^-$）が存在し（Fig. 1）、(1)式の電気化学反応が 100 %に近いクーロン効率で進行する [1]。

$$4[Al_2Cl_7]^- + 3e^- \rightleftharpoons Al + 7[AlCl_4]^- \qquad (1)$$

同様の結果が、他の金属塩化物塩を用いたイオン液体で得られることも多いが [2]、これを負極反応に利用したときに得られるメリットを考慮すると、その対象は安価で理論容量が大きな Al および Zn となる。$AlCl_3$–[C_2mim]Cl や $ZnCl_2$–[C_2mim]Cl を電解液に用いると、Al や Zn の金属負極反応が利用可能となるため、これらの電解液で使うことのできる正極反応の探索がこの分野での主たる検討課題である [3-7]。これらの電池系は電極反応に関与するイオン種が全て錯アニオンであることから、多価金属負極アニオン電池に分類される。本講演では、安価な多価金属（Al, Zn）負極を用いたアニオン電池の研究開発状況について概説する。

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