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Preparation of the Lithium Ion Permeable Film Containing Crown Ether for Lithium-Air Battery

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Introduction

Li-air battery can theoretically store 5-10 times higher energy than current batteries, so it's expected to be as a future energy storage system. Li-air battery is composed of Li metal anode, organic electrolyte, and a porous cathode. Cathode active material is O_2 in ambient air. During discharge reaction, lithium dissolves in anode, lithium per oxide is formed on the cathode. For practical use, Lithium air battery has problems such as rechargeability, high charging overpotential, and corrosion of Li metal by moisture from ambient air. In particular, corrosion of Li metal by moisture is one of the serious problem because it makes battery life shorter. In this work, Li ion selective permeable film containing crown ether as the ion permeable material was prepared. Moreover, Li-air battery was evaluated using the prepared film in order to prevent H_2O invasion by moisture.

Experimental

Sample film was prepared by drying the tetrahydrofuran (THF) solution containing Crown ether, LiTFSI, plasticizer, and polyvinyl chloride (PVC). Benzo-12-crown-4-ether was chosen for Li ion permeable material. Ionic conductivity was measured by electrochemical impedance spectroscopy (EIS). Frequency range and zero to peak amplitude were 1 MHz-10 mHz and 10 mV, respectively. Battery performance of the film was investigated using 2032 type coin cell assembled Li metal/1M LiTFSI in DMSO/KB on carbon paper coated permeable film in a glove box filled with pure argon. Charge-discharge test was performed at 100 μA cm^{-2} and 500 mAh g^{-1} in ambient air.

Results and Discussion

First, preparation of Li ion selective permeable film containing crown ether as the ion permeable material was performed. High ionic conductivity of the film was obtained using crown ether, and the conductivity was depended on the kind of the plasticizer. The film containing NPOE as a plasticizer showed high ionic conductivity of 8.09×10^{-6} S cm^{-1}. This ionic conductivity was 16 times as high as any other plasticizer used for PVC. Because of NPOE's high dielectric constant, conformation reconfiguration energy of crown ether was decreased when it takes Li ion.

Second, cycle performance of Li-air battery using the prepared film was investigated. Fig.1 (a), (b) shows cycle performance of Li-air batteries with or without NPOE-containing film in ambient air. A low capacity of both batteries was observed at early cycles, and these cycles mean state of aging process of the permeable films. Only 3 cycles from 12th cycle to 14th cycle was attained when the Li-air battery was consisted without permeable film. On the contrary, 12 cycles from 19th cycle to 30th cycle was attained when Li-air battery was consisted with permeable film. The cycle performance of the Li-air battery was improved by using the Li ion permeable film with crown ether. It was supposed that this improvement was realized by prevention of H_2O invasion by the prepared film.

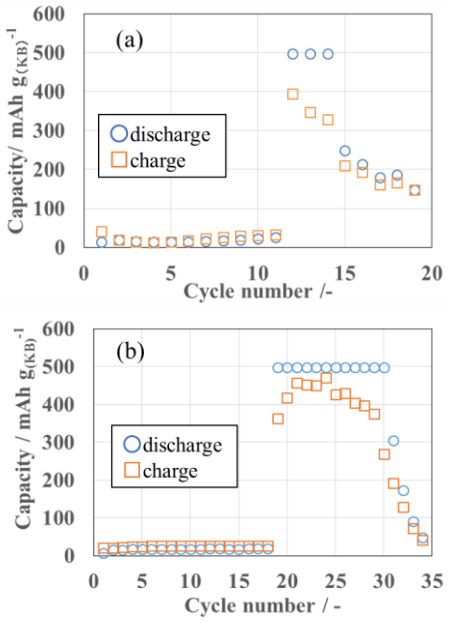

Fig.1 (a) Cycling performance without film, (b) with film contained crown ether

Reference:

[1] T. Osaka, T. Momma, K. Nishimura, S. Kakuda, *J. Electrochem. Sci.*, **141**.8 (1994).