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学 位 論 文 内 容 の 要 旨

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Mechanistic Study on Lithium–Oxygen Battery-Degradation Mechanism in TEGDME
Solution by Mass Spectrometry
(質量分析による TEGDME 溶液中のリチウム酸素電池の劣化メカニズムに関する機構的研究)

A rechargeable lithium-air battery (LAB) is considered to be one of the most promising energy storage devices because of its large theoretical energy density. Despite significant efforts by many research groups, LAB is still far from practical use and many problems must be overcome. The first problem is associated with the use of air as it contains many components other than oxygen including N_2 , H_2O , and CO_2 , which interfere battery reactions. Thus, most of the fundamental studies are not on LAB but on Lithium-oxygen battery (LOB), which uses pure oxygen as an active material. Even LOB has many serious problems, including low cyclability caused by (1) high charging overpotential, which induces degradation of positive electrode (carbon) and electrolyte solution, and (2) degradation/dendrite formation of negative Li metal electrode. To improve cyclability, it is essential to clarify the mechanism of degradation of electrodes and electrolytes.

In this thesis, a custom-made test cell equipped with a gas inlet and outlet was assembled in a dry booth (dew point less than $-90^\circ C$) in a dry-room by stacking a Li metal foil and a polyethylene membrane, on top of which 15 μL of the 1 M LiTFSI TEGDME solution was placed, followed by a carbon nanotube (CNT)-based porous carbon sheet (KJCNT), a stainless steel mesh, and a conductive spring to provide the cell assembly with a pressure of 35 kPa. After assembly, the cell was connected to an Ar/O₂ line (1 atm), electrochemical controllers, and the MS systems. The degradation mechanism of TEGDME-based LOB was investigated in-situ using on-line QMS and CTPC-GC/MS, and ex-situ post-analysis of organic compounds, which were collected by adsorption in small columns during the discharge and charge, using TSP-GC/MS. The on-line QMS was used to monitor mass signals of mass numbers between 12-120 during the charging process. CTPC-GCMS and TSP-GC/MS were executed to collect products with large mass numbers in both discharge and charge processes.

In Chapter 1, the fundamental, including lithium anode, electrolyte, and cathode, evolution, and challenges of LOB are introduced. The characterization tools for LOB mechanism study are briefly reviewed.

In Chapter 2, experimental details, including chemicals, materials, cell assembly, and information on equipment are provided. The theoretical information of various mass spectrometers is also provided.

In Chapter 3, on-line QMS and TSP-GCMS were employed for real-time monitoring of generated gaseous products during charging. To qualitatively understand the energetics of the product formation during the charging process, a linear voltage sweep (LSV: 0.05 mV s⁻¹) and voltage step modes were employed in addition to constant current charging. The presence of two distinctly different types of Li_2O_2 , one being decomposed in a wide range of relatively low voltages (2.8–4.6 V) (l- Li_2O_2) and the other being decomposed at higher voltage of around 4.6 V (h- Li_2O_2), was confirmed by both LSV and step experiments. H_2O generation begins when O_2 generation reaches its peak, and it was found that approximately 50% of the O atom in H_2O originate from the discharge gas, while the remaining 50% originate from solvent decomposition and the initial water content in the electrolyte. CO_2 generation took place accompanied by the decomposition of h- Li_2O_2 , and around 70% O atom in CO_2 originated from the discharge gas, the 30% originated from the solvent decomposition.

In Chapter 4, on-line QMS was introduced combining with isotope experiments, to

follow and analyze products generated during the charging process. $^{12}\text{CD}_3$ _TEGDME, $^{13}\text{CH}_3$ _TEGDME and $^{12}\text{CH}_3$ _TEGDME were used as solvent, and $^{18}\text{O}_2$ and $^{16}\text{O}_2$ were used as the discharge gas. A total of 17 compounds were identified as the battery reaction products by mass spectrometry. From the detected products, battery degradation products can be divided into two types: generates from high overpotential induced degradation reactions (electrochemical reactions), such as 1,4-Dioxane, Methylal, and Methoxyethene, and active species triggered decomposition reactions (chemical reactions), such as Methanol, Ethanol, etc. Notably, some degradation products are generated by both of the two reactions, such as Methyl formate.

In Chapter 5, on-line CTPC-GC/MS system was constructed to detect reaction products of LABs during discharge and charging in real-time with high accuracy. During cell operation, the generation of organic molecules was tracked over time by repeatedly sampling the cell's headspace gas for very short periods of time, such as 15 s, and for a fixed period of time, such as 40 min. By controlling the sampling time and period, the loss of generated molecules by gas flow can be minimized. The CTPC-GC/MS system was operated under constant-current discharge and constant-current or voltage-sweep charging. A total of 37 peaks were detected and 27 of them were assigned to specific molecules. Several molecules were present as impurities in TEGDME even before discharge and a few molecules were generated during discharge but most of the molecules were generated during charging. The results obtained under voltage scan without discharge showed that some of the molecules generated at the end of charging were also generated without discharge, indicating these molecules were formed by direct electrochemical oxidation without involvement of reactive oxygen species.

Degradation of TEGDME in LOB during discharge/charge was investigated by monitoring the generation and decomposition of molecules in real-time by mass spectrometry systems. Most of the molecules were generated during charge as a result of the degradation of TEGDME by reactive oxygen species and electrochemical oxidation. These molecules were decomposed during discharge by reactive oxygens. In the future, (1)more molecules assignment will be kept on going for more detailed degradation mechanism, and mass spectrometry systems were committed to applying to the degradation of various electrolytes. (2)Researches on the effect of various additives and singlet oxygen quenchers in inhibiting battery degradation will be conducted. (3)Many ex-situ and operand techniques such as SEM, TEM, XPS, surface enhanced Raman scattering (SERS), etc. will be introduced into subsequent studies to characterize the reaction mechanism of the cell more intuitively.