HOKKAIDO UNIVERSITY

Title	Effect of Lithium Salt Concentration on Interfacial Solvation Structure and Electrochemical Oxygen Reduction for Nonaqueous Li-O2 Battery [an abstract of dissertation and a summary of dissertation review]
Author(s)	,
Citation	. ( ) 14464
Issue Date	2021-03-25
Doc URL	http://hdl.handle.net/2115/81409
Rights(URL)	https://creativecommons.org/licenses/by/4.0/
Type	theses (doctoral - abstract and summary of review)
Additional Information	There are other files related to this item in HUSCAP. Check the above URL.
File Information	WANG_LEI_abstract.pdf ( )

学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（理学）　　氏名　王　磊

学 位 論 文 題 名

Effect of Lithium Salt Concentration on Interfacial Solvation Structure and
Electrochemical Oxygen Reduction for Nonaqueous Li-O$_2$ Battery
（非水系 Li-O$_2$ 電池の界面溶媒和構造と電気化学的酸素還元に及ぼすリチウム塩濃度の影響）

Nonaqueous lithium oxygen (Li-O$_2$) battery is used as a substitute for lithium-ion batteries in electric vehicles because of its extremely high theoretical specific capacity (3860 mAh g^{-1}). However, due to its low cycle efficiency, Li-O$_2$ battery has not yet been commercialized, although they have been studied for more than two decades. Recently, the use of superconcentrated electrolyte has been proven to greatly improve the cycle efficiency of Li-O$_2$ battery because it can stabilize lithium metal anodes. However, the stabilization mechanism of superconcentrated electrolyte for lithium metal anodes, especially the molecular explanation, such as the solvation structure on the electrode/electrolyte interface, has not been well understood. The properties of the electrolyte, mainly the donor number of the solvent and the lithium salt anion, are considered to be the key factors affecting the oxygen reduction reaction mechanism at the cathode, thereby affecting the battery capacity. Therefore, the influence of lithium salt concentration on oxygen reduction at the cathode under solvents with different donor number needs to be revealed as well.

The objective of this thesis is to: (1) investigate the concentration-dependence of solvation structure at gold/electrolyte interface in two different electrolytes system using surface enhanced Raman spectroscopy (SERS), and (2) the oxygen reduction mechanism on gold model cathode affected by lithium salt concentration in DMSO and TEGDME solutions, using in situ SERS, electrochemical quartz crystal microbalance (EQCM) and rotating ring/disk electrodes (RRDE).

In Chapter 1, the backgrounds of the lithium-based secondary batteries and general electrode reaction mechanism for the nonaqueous Li-O$_2$ battery are briefly reviewed. The challenges faced by the nonaqueous Li-O$_2$ battery, including Li anode, cathode and electrolyte are given. Superconcentrated electrolytes for Li-O$_2$ battery are also reviewed.

In Chapter 2, the experimental details are given, including the materials, electrochemical measurements, characterization techniques and electrode potential calibration.

In Chapter 3, SERS was used to detect solvation structure at the electrode/electrolyte interface in $LiNO_3$-DMSO and LITFSI-DMSO solutions with various lithium salt concentrations. DMSO molecules were found to interact with the gold substrate and form Au-O and Au-S bonds, while $TFSI^-$ was adsorbed by the formation of Au-O bonds. However, there is no indication that NO_3^- interacts with gold through chemical adsorption. In the superconcentrated LITFSI-DMSO electrolytes, chemisorbed $TFSI^-$ is the only species on the gold surface, while NO_3^- and $Li(DMSO)_3^+NO_3^-$ complex is dominant in superconcentrated $LiNO_3$-DMSO solutions. A high proportion of salt anion ($TFSI^-$ and NO_3^-) dominant gold surface in superconcentrated DMSO electrolytes might benefit for the formation of SEI-derived from salt anion, which is the reason for good battery cycle performance.

In Chapter 4, in situ SERS and EQCM in combination with RRDE measurements were utilized to reveal the oxygen reduction reaction (ORR) mechanism for various concentration of $LiNO_3$-DMSO solutions. It turns out that the effect of $LiNO_3$ concentration on ORR mainly achieved by affecting the O_2^- absorbed on the electrode surface and LiO_2 dissolution into bulk electrolyte, which is the intermediate for surface and solution pathway, respectively. It shows that the O_2^- adsorbed on electrode surface in low concentration is much higher than that in medium concentration, which allow for more O_2^- to be reduced into Li_2O_2 in low concentration. While in the high-concentrated electrolyte, due to the high viscosity of the electrolyte, a large amount of O_2^- is concentrated on the electrode surface, eventually failed to form Li_2O_2.

In Chapter 5, the effect of $LiNO_3$ concentration on ORR mechanism in Li^+-TEGDME solutions was investigated by RRDE and EQCM measurement. It shows that the LiO_2 solubility decrease with $LiNO_3$ concentration. EQCM measurements shows that $LiNO_3$ concentration has almost no effect on the surface electrode reaction. O_2 was firstly electrochemically reduced into LiO_2 and leave electrode surface at low overpotential. At medium overpotential, O_2 is mainly converted to Li_2O_2 through surface two-electron reduction pathway, together with small part of LiO_2 dissolute into electrolyte. At high overpotential, oxygen is found to be reduced into LiO_2 on the surface of Li_2O_2.

In Chapter 6, the general conclusion of this thesis and future prospects are given.