## Electrochemical reduction of oxygen in organic solvents with and without Li<sup>+</sup> cation – Effect of oxygen supply <u>Xiao Jie</u> and Kohei Uosaki Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN) National Institute for Materials Science (NIMS) Tsukuba 305-0044, Japan

Li-air battery has attracted much attention as their theoretical energy density is extremely high compared with those other rechargeable batteries [1]. Unfortunately, however, the understanding of the mechanism and of electrochemical deposition/dissolution kinetics reactions of Li-O<sub>2</sub> species is still limited [2, 3], and very low reversibility of these reactions inhibits the development of Li-air battery. Currently, many studies are being carried out on the effects of the solvents, electrolytes and electrode materials on the kinetics and reversibility of the reactions to obtain fundamental information for a stable reaction system should be established. One of the problems of these studies is the difference in the supply of oxygen between gas-diffusion electrode, i.e., Li-air battery cathode, and disk electrode usually used in fundamental study.

Here we employed two electrode configurations, namely ordinary and hanging meniscus configurations, to investigate the oxygen reduction reaction in various NNsolvents such as acetonitrile (AN), dimethylformamide (DMF), dimethylsulfoxide (DMSO) and tetraethylene glycol dimethyl ether (TEGDME) with and without Li<sup>+</sup> cation so that the supply of oxygen to the electrode can be controlled. It is expected that the supply of oxygen to the electrode can be enhanced by using the hanging meniscus configuration of electrode since the three-phase, gas/solution/electrode, boundary (TPB) can provide large mount of oxygen [4] as shown in Figure 1. Figure 1. Schematic representation of the working area of (a) ordinary and (b) hanging meniscus configurations.

Figure 2 shows CVs of (a) a Au disk electrode ( $\phi = 3.0$  mm) with sealed side wall in the ordinary configuration and (b) a Au disk electrode ( $\phi = 2.8$  mm) without sealing in the meniscus configuration in oxygen saturated AN (solid line), DMF (broken line), and DMSO (dotted line) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>). CVs were not obtained in TEGDME without Li<sup>+</sup> ion as the solubility of TBAPF<sub>6</sub> in



TEGDME was very low. The CVs of the Au electrode in the ordinary configuration (Fig. 2(a)) show both cathodic and anodic peaks with the former being slightly larger than the latter, confirming that oxygen is reduced initially to superoxide ion via one-electron quasi-reversible step, as already reported [5]. Peak currents are in the order of DMSO<DMF<AN, reflecting the solvent dependent solubility and diffusion coefficient of oxygen. Peak separations are in the order of DMSO<DMF<AN.



Figure 2. CVs of (a) a Au disk electrode ( $\phi = 3.0$  mm) with sealed side wall in the ordinary configuration and (b) a Au disk electrode ( $\phi = 2.8$  mm) without sealing in the meniscus configuration in oxygen saturated AN (solid line), DMF (broken line), and DMSO (dotted line) containing 0.1 M tetrabutylammonium hexafluoro-phosphate (TBAPF<sub>6</sub>). Sweep rate: 100mV/s.

The CVs of the Au electrode in the meniscus configuration (Fig. 2(b)) are totally different from those in the ordinary configuration. Much larger cathodic current without noticeable peak was observed, reflecting the enhanced supply of  $O_2$  to the electrode through the  $O_2$  gas/Au/solution three-phase boundary (TPB). Linear increase of the current at large overpotential region shows IR limited current and solvent dependent slope (DMSO<DMF<AN) can be explained by the difference in the conductivity [6]. It should be noticed that no anodic current was found in the AN solution.

Similar measurements were carried out at Au electrode in the two configurations in various solvents containing  $Li^+$  ion and at carbon electrode in the two configurations in various solvents with and without  $Li^+$  ion and the results are compared with those mentioned above.

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