A Study of e⁻ Transport through Li₂O₂, the Main Discharge Product in the Li-O₂ Battery

In the field of energy storage devices the pursuit for cheap, high energy density, reliable secondary batteries is at the top of the agenda. The Li-O₂ battery is one of the possible technologies that, in theory, should be able to close the gap, which exists between the present state-of-the-art Li-ion technologies and the demand placed on batteries by technologies such as electrical vehicles [1]. However, the Li-O₂ battery still suffers greatly from high overpotentials during oxygen reduction and evolution reactions (discharge and charge, respectively), poor rechargeability, and decomposition of salts and solvents etc. [2] [3]. In order to improve the electrochemical performance of the Li-O₂ batteries; it is crucial to understand the fundamental mechanisms that governs and limits the system during electrochemical operation. Here we present a redox probing study of the charge transfer across the deposition product lithium peroxide, Li₂O₂, using outer-sphere redox shuttles: cobaltocene, ferrocene, and decamethylferrocene. The change in heterogeneous electron transfer exchange rate as a function of the potential and the Li₂O₂ layer thickness (~state of charge) was determined using electrochemical impedance spectroscopy. The attenuation of the electron transfer exchange rate with film thickness is dependent on the probing potential, indicating that hole tunneling is the dominant process for charge transfer through Li₂O₂ supporting previous work by Luntz et al. [4]. Additionally, this work includes the determination of diffusion coefficients and concentrations of the redox shuttles and the superoxide ion, in a 1,2-dimethoxyethane based electrolyte. References [1] S. A. Freunberger, P. G. Bruce, L. J. Hardwick et J.-M. Tarascon, «Li-O₂ and Li-S batteries with high energy storage,» Nature Materials, vol. 11, pp. 19-29, 2012. [2] B. D. McCloskey, A. Valery, A. C. Luntz, S. R. Gowda, G. M. Wallraff, J. M. Garcia, T. Mori et L. E. Krupp, «Combining Accurate O₂ and Li₂O₂ Assays to Separate Discharge and Charge stability Limitations in Nonaqueous Li-O₂ Batteries,» J. Phys. Chem. Lett., vol. 4, pp. 2989-2993, 2013. [3] R. Younesi, M. Hahlin, F. Björefors et K. Edström, «Li-O₂ Battery Degradation by Lithium Peroxide (Li₂O₂): A Model Study,» Chem. Mater., vol. 25, pp. 77-84, 2013. [4] A. C. Luntz, V. Viswanathan, J. Voss, J. B. Varley, J. K. Nørskov, R. Scheffler and A. Speidel, "Tunneling and Polaron Charge Transport through Li₂O₂ in Li-O₂ Batteries," J. Phys. Chem. Lett., vol. 4, pp. 3494-3499, 2013.