

Stoichiometric analysis of Li_2O_2 stored in Li-O₂ batteries

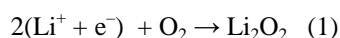
Yoko Hase,¹ Emi Ito,¹ Tohru Shiga,¹ Fuminori Mizuno,^{2,3} Hidetaka Nishikoori,³ Hideki Iba³ and Kensuke Takechi¹

¹Energy Creation & Storage Division, Toyota Central R&D Labs., Inc., 41-1 Yokomichi, Nagakute, Aichi 480-1192, JAPAN

²Materials Research Department, Toyota Research Institute of North America, 1555 Woodridge Ave., Ann Arbor, MI 48105

³Battery Research Division, Toyota Motor Corporation, 1200 Misyuku, Susono, Shizuoka 410-1193, JAPAN

Li-O₂ batteries is one of the promising candidates to meet the demand for future vehicles, electronics and many other applications due to their high theoretical storage capacity^[1]. In this battery, it is well known that Li_2O_2 is produced as discharge product according to Equation (1) below, with its reverse reaction occurring on charge.



Recently, we have explored the solvents for the electrolyte which are stable under Li_2O_2 generation reaction. A kind of quaternary ammonium-based ionic liquid such as *N,N*-diethyl-*N*-methyl-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSA) is found to be one of the suitable solvent for the electrolytes of Li-O₂ batteries and we identified Li_2O_2 as the primary product after initial discharge^[2]. Unfortunately, the charge capacity is limited to approximately 80% of discharge.

The reduced capacity of Li-O₂ batteries on cycling is a continuing problem, and its cause is currently the focus of a number of research groups^[3]. For better understanding of discharge reactions and irreversibility on charging of Li-O₂ batteries incorporating DEME-TFSA electrolyte, we demonstrate a novel analytical technique capable of quantifying Li_2O_2 via its selective oxidative reaction with an oxoammonium cation (Figure 1). The cation is synthesized from 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO), which is chemically stable and oxidized to the corresponding oxoammonium cation (TEMPO⁺) via chemical or electrochemical oxidation.

To verify the concept of Li_2O_2 quantitation, stoichiometric analysis was conducted using spectroscopic methods. The reaction of TEMPO⁺ClO₄⁻ and Li_2O_2 reagent was performed in acetonitrile under an inert atmosphere at 25 °C. Along with the reaction process, the loss of Li_2O_2 was observed, while O₂ evolution was followed by gas chromatography/mass spectrometry. IR spectrum of the reaction products is almost identical to that of pure TEMPO and LiClO₄ (Figure 2). This result suggests that Li_2O_2 underwent oxidation with simultaneous reduction of TEMPO⁺. The reactivity of Li_2O_2 was also estimated by means of the conversion ratio from TEMPO⁺ to TEMPO. As a result, Li_2O_2 was found to be stoichiometrically oxidized by TEMPO⁺ClO₄⁻.

Subsequently, the quantities of Li_2O_2 stored in the cathode were determined by reductive reaction of

TEMPO⁺. In this presentation, we report the results of the quantitative evaluations. The causes of low coulomb efficiency of the Li-O₂ batteries will also be discussed.

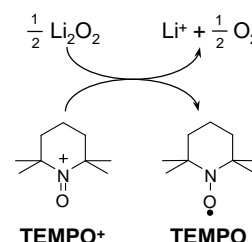


Figure 1. Oxidation of Li_2O_2 by TEMPO⁺.

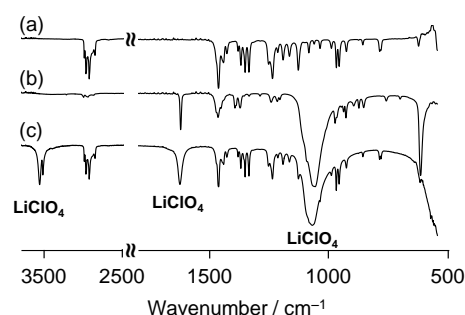


Figure 2. IR spectra of (a) TEMPO, (b) TEMPO⁺ClO₄⁻, and (c) reaction products between TEMPO⁺ClO₄⁻ and Li_2O_2 ($[\text{TEMPO}^+\text{ClO}_4^-]/[\text{Li}_2\text{O}_2] = 2$).

[1] K. M. Abraham, Z. Jiang, *J. Electrochem. Soc.* **1996**, *143*, 1-5.; T. Ogasawara, A. Debart, M. Holzapfel, P. Novak, P. G. Bruce, *J. Am. Chem. Soc.* **2006**, *128*, 1390–1393.

[2] S. Higashi, Y. Kato, K. Takechi, F. Nakamoto, F. Mizuno, H. Nishikoori, H. Iba, T. Asaoka, *J. Power Sources* **2013**, *240*, 14–17.

[3] Y. Chen, S. A. Freunberger, Z. Peng, F. Barde, P. G. Bruce, *J. Am. Chem. Soc.* **2012**, *134*, 7952–7957.; B. D. McCloskey, R. Scheffler, A. Speidel, D. S. Bethune, R. M. Shelby, A. C. Luntz, *J. Am. Chem. Soc.* **2011**, *133*, 18038–18041.; R. Black, S. H. Oh, J.-H. Lee, T. Yim, B. Adams, L. F. Nazar, *J. Am. Chem. Soc.* **2012**, *134*, 2902–2905.; M. M. O. Thotiyl, S. A. Freunberger, Z. Peng, P. G. Bruce, *J. Am. Chem. Soc.* **2013**, *135*, 494–500.; F. Mizuno, K. Takechi, S. Higashi, T. Shiga, T. Shiotsuki, N. Takazawa, Y. Sakurabayashi, S. Okazaki, I. Nitta, T. Kodama, H. Nakamoto, H. Nishikoori, S. Nakanishi, Y. Kotani, H. Iba, *J. Power Sources* **2013**, *228*, 47–56.