Stoichiometric analysis of Li₂O₂ stored in Li₂O₆ batteries

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Li₂O₂ batteries are one of the promising candidates to meet the demand for future vehicles, electronics and many other applications due to their high theoretical storage capacity.⁴ In this battery, it is well known that Li₂O₂ is produced as discharge product according to Equation (1) below, with its reverse reaction occurring on charge.

\[ 2\text{Li}^+ + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2 \quad (1) \]

Recently, we have explored the solvents for the electrolyte which are stable under Li₂O₆ 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 Li₂O₂ batteries and we identified Li₂O₆ as the primary product after initial discharge.¹ Unfortunately, the charge capacity is limited to approximately 80% of discharge.

The reduced capacity of Li₂O₂ batteries on cycling is a continuing problem, and its cause is currently the focus of a number of research groups.⁵ For better understanding of discharge reactions and irreversibility on charging of Li₂O₂ batteries incorporating DEME-TFSA electrolyte, we demonstrate a novel analytical technique capable of quantifying Li₂O₂ via its selective oxidative reaction with an oxoammonium cation (Equation 1). The cation is synthesized from 2,6,6-tetramethylperidinyl-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 Li₂O₂ quantitation, stoichiometric analysis was conducted using spectroscopic methods. The reaction of TEMPO⁺ClO₄⁻ and Li₂O₂ reagent was performed in acetonitrile under an inert atmosphere at 25 °C. Along with the reaction process, the loss of Li₂O₂ 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 Li₂O₂ underwent oxidation with simultaneous reduction of TEMPO⁺. The reactivity of Li₂O₂ was also estimated by means of the conversion ratio from TEMPO⁺ to TEMPO. As a result, Li₂O₂ was found to be stoichiometrically oxidized by TEMPO⁺ClO₄⁻.

Subsequently, the quantities of Li₂O₂ 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 Li₂O₂ batteries will also be discussed.