X-Ray Acceleration On Electrochemical Reaction

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X-ray acceleration on electrochemical reaction

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In most photo-electrochemical systems, photoactive materials generate charge carriers and/or play catalytic role in the reaction, their composition will not be changed after each cycle of interactions [1,2]. However, photo energy can also speed up electrochemical formation, transformation, and decomposition of materials that is sensitive to the incident light. Studying the effect of electromagnetic irradiation on electrochemical reactions can provide the mechanism details in these reactions, and extend the applications of these reactions. Here, in situ synchrotron radiation powder X-ray diffraction (SR-PXD) was used to explore the influence of X-ray irradiation on the Li_2O_2 decomposition during charging processes of Li-O_2 cell. Synchrotron based X-ray radiation acted as both the light source to accelerate Li_2O_2 electrochemical decomposition and the tool to continuously track this process. The effects of X-ray intensity and charge potential on the kinetics of Li_2O_2 electrochemical decomposition were systematically investigated. The X-ray acceleration mechanism of Li_2O_2 electrochemical decomposition was proposed. Our study contributes to the understanding of the limiting factors in Li_2O_2 electrochemical decomposition, which is significant for its applications (e.g. in Li-air battery).

Fig. 1 shows in situ XRD patterns of Li_2O_2-based electrode collected every 10 min during charging with a constant current. Si and Li_2O_2 crystalline phases were clearly observed. Silicon was used as a standard substance to calibrate the amount of Li_2O_2. The considerable decrease in Li_2O_2 peak intensity confirms the fast decomposition of Li_2O_2 during charging process. The residual ratio of Li_2O_2 revealed a reduction to 50% after 110 min charging, which shows much faster decomposition than that without X-ray irradiation (<5%). Therefore, it can be concluded that X-ray irradiation accelerates electrochemical decomposition of Li_2O_2.

The decomposition curves of Li_2O_2 charged at a constant current with different intensities of X-ray irradiations are presented in Fig. 2. It can be seen that the residual ratio of Li_2O_2 reduced to 50% with I_a and 66% with I_b after 110 min charging, respectively, which indicates the intensity of X-ray irradiation influences the rate of Li_2O_2 decomposition. To investigate the relationship between intensity of X-ray and the rate of Li_2O_2 decomposition, the kinetic values are estimated by linear curve fitting (30 min$\leq$ t $\leq$ 100 min) of Li_2O_2 decomposition. The decomposition rate constant under the low intensity X-ray irradiation (k_b=0.46 min^{-1}) is 68.4% of that under the high intensity X-ray irradiation (k_a=0.67 min^{-1}), which exhibits a proportional relationship to the intensity of X-ray used.

In order to examine whether the X-ray is the only factor on the decomposition of Li_2O_2 here, the decomposition of Li_2O_2 was sequentially performed at constant potential of 3.8 V and 4.2 V for 120 min each, as shown in Fig.3. There is only 2.6% of Li_2O_2 decomposed when the battery charged at the constant potential of 3.8 V for 2 h, while the residual Li_2O_2 is reduced to 45.8% after charging at 4.2 V. The huge difference of decomposition rates at 3.8 V (k_a'=0.015 min^{-1}) and 4.2 V (k_b'=0.413 min^{-1}) indicates the existence of threshold potential for Li_2O_2 electrochemical decomposition. Therefore, both X-ray and external potential play an important role in the accelerated Li_2O_2 electrochemical decomposition.

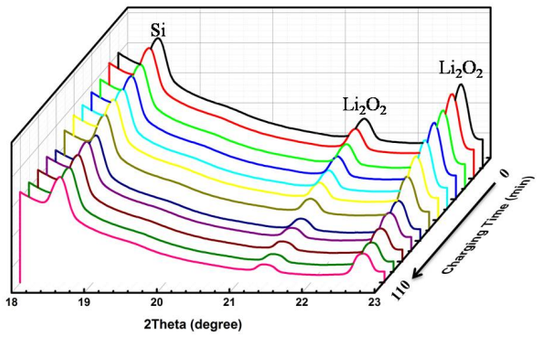

Figure 1. In situ XRD patterns of Li_2O_2-based electrode collected every 10 min during charging process with a constant current.

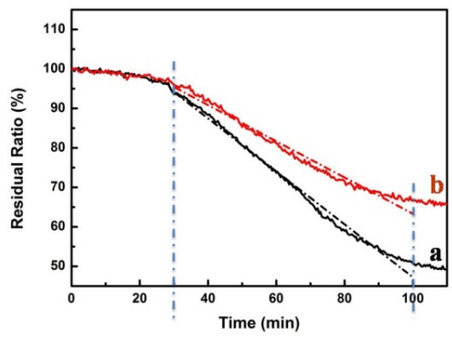

Figure 2. The curves (solid line) and linear curve fittings (dash line) of Li_2O_2 decomposition in the electrode charged at a constant current under different intensities of the X-ray irradiation (a) I_a, and (b) I_b (I_b= 68% I_a)

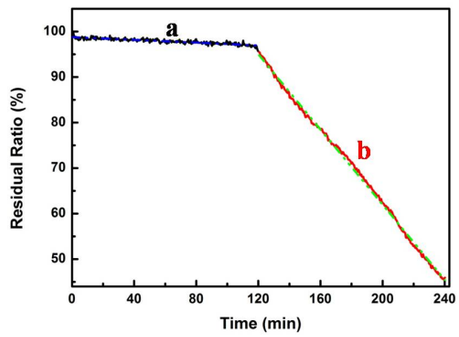

Figure 3. The curves (solid line) and linear curve fittings (dash line) of Li_2O_2 decomposition in the electrode at constant potentials of (a) 3.8 V and (b) 4.2 V

References:

1. Fujishima, A. and K. Honda, *Electrochemical Photolysis of Water at a Semiconductor Electrode.* Nature, 1972. 238(5358): p. 37-38.
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