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 can provide the mechanism details in these reactions, and extend the applications of these reactions. Here, in situ was used to explore the influence of X-ray irradiation on electrochemical reactions, and electromagnetic irradiation on electrochemical reactions after each cycle of interactions [1, 2]. However, photo sensitive to the incident light. Studying the effect of transformation, and decomposition of materials that is energy can also speed up electrochemical formation, residual ratio of Li$_2$O$_2$ decomposition was proposed. Our study contributes to the understanding of the limiting factors in Li$_2$O$_2$ electrochemical decomposition, which is significant for its applications (e.g. in Li-air battery).

Fig. 1 shows in situ XRD patterns of Li$_2$O$_2$-based electrode collected every 10 min during charging with a constant current. Si and Li$_2$O$_2$ crystalline phases were clearly observed. Silicon was used as a standard substance to calibrate the amount of Li$_2$O$_2$. The considerable decrease in Li$_2$O$_2$ peak intensity confirms the fast decomposition of Li$_2$O$_2$ during charging process. The residual ratio of Li$_2$O$_2$ 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$_2$O$_2$.

The decomposition curves of Li$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$ decomposition. To investigate the relationship between intensity of X-ray and the rate of Li$_2$O$_2$ decomposition, the kinetic values are estimated by linear curve fitting (30 min ≤ t ≤ 100 min) of Li$_2$O$_2$ decomposition. The decomposition rate constant under the low intensity X-ray irradiation ($k_a$=0.46 min$^{-1}$) is 68.4% of that under the high intensity X-ray irradiation ($k_b$=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$_2$O$_2$ here, the decomposition of Li$_2$O$_2$ 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$_2$O$_2$ decomposed when the battery charged at the constant potential of 3.8 V for 2 h, while the residual Li$_2$O$_2$ 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$_2$O$_2$ electrochemical decomposition. Therefore, both X-ray and external potential play an important role in the accelerated Li$_2$O$_2$ electrochemical decomposition.

References: