Kyushu Synchrotron Light Research Center

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Experiment Report for Prefectural Beamline

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Beamline no.: BL12
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Li-O_2電池における Li-O_2電気化学反応生成物のX線光電子分光分析

XPS analysis of lithium peroxide, carbonate and carboxylates for reference of Li-O_2 electrochemical reaction product for Li-O_2 battery

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１． Summary（Note: Please include conclusions）

We obtained Li 1s and O 1s XPS spectra of Li_2O_2, Li_2CO_3, LiOH, $LiCO_2H$, and $LiCO_2CH_3$ powders at BL12 of SAGA-LS, which would be used for reference data of real Li–O_2 reaction products (proposal no. 1310118PT).

２． Purpose of experiment and background

The purpose of this project is to acquire Li 1s and O 1s X-ray photoelectron spectroscopy (XPS) data of Li_2O_2, Li_2CO_3, LiOH, $LiCO_2H$, and $LiCO_2CH_3$ powders. These XPS data will be used for the reference of Li-O_2 reaction products, obtained in Li-O_2 battery (proposal no. 1310118PT).

３． Experimental（Note: Description of sample, method of experiment and analysis, etc.）

We prepared the following 5 powders (table).

No.	Sample name	Purity	Preparation
1	Li_2O_2	99%	The powders completely dried in vacuum oven were loaded on the XPS stage using double-side carbon tape in Ar
2	Li_2CO_3	99%	
3	LiOH	98%	

4	$LiCO_2H$	98%	gas-filled glove box.
5	$LiCO_2CH_3$	99%	

The powders were very thinly pasted on a double-side carbon tape in an Ar-filled glove box and directly transferred to XPS chamber using a hermetic Ar-filled transfer vessel to avoid air exposure. The synchrotron XPS measurements were performed using a photon energy of 650 eV and a base pressure of 10^{-8} Pa. The XPS data were calibrated by the carbon-related peak obtained from the carbon tape.

4. Results and Discussions

Since the insulating lithium-related powders generate the large charging effect, the XPS peaks were largely shifted. These peaks were corrected by the calibration as referring to carbon (285.66 eV) acquired from the double-side carbon film underneath the powders. In addition, the small ejected photoelectron current (I_s) from the insulating powder samples resulted in low signal to noise ratio of spectra peaks despite with many scanning numbers. Figure 1 shows the resultant XPS spectra of O 1s and Li 1s binding energy (BE) regions. The Li_2O_2 has a symmetric O 1s peak at 532.5 eV and Li 1s peak at 55.9 eV. The LiOH has a similar O 1s peak to the Li_2O_2, i.e., 532.6 eV, whereas a Li 1s peak is slightly different, showing at 55.0 eV. The Li_2CO_3 has an asymmetric O 1s peak at 533.6 eV and a broad Li 1s peak at 56.7 eV. The lithium carboxylates (Li_2CO_2H and $Li_2CO_2CH_3$) powders have very broad O 1s peaks in 532-534 eV and negligible Li 1s peak even more than 100 times scan. The large charge effect hindered to obtain clear lithium carboxylates spectra using the XPS.

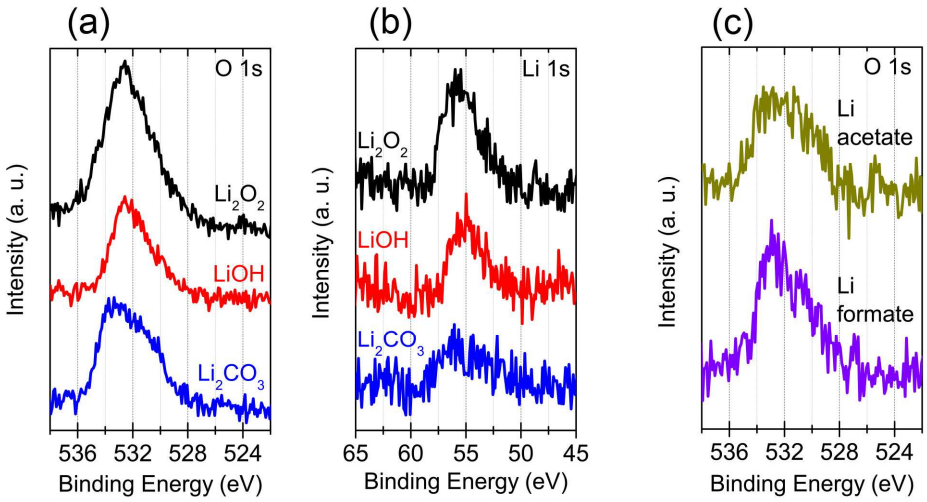

Figure 1. XPS spectra of (a) O 1s, (b) Li 1s Li_2O_2, LiOH, and Li_2CO_3, and (c) O 1s of $LiCO_2H$ and $LiCO_2CH_3$.

5. Future issues

Identifying chemical information of real Li–O_2 reaction products (proposal no. 1310118PT) by referring to these powder XPS data.

6. References

None

7. Publications, patents (Note: Typical deliverables related to this proposal.)

Publication: Rui Wen and Hye Ryung Byon, "In situ monitoring of the Li-O_2 electrochemical reaction on nanoporous gold using electrochemical AFM", *Chemical Communications*, **2014**, *50*, 2628-2631.

8. Keywords (Note: 2-3 words about samples and experimental methods.)

Lithium-related compounds, Li-O_2 battery, XPS

９．About the publication of research results

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