

# ZrO<sub>2-x</sub> surface modification on LiCoO<sub>2</sub> film using arc plasma deposition

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Surface modification of ZrO<sub>2</sub> on LiCoO<sub>2</sub> cathodes is an effective way to stabilize the cathode/electrolyte interfaces during high-voltage (> 4.2 V) operation of lithium ion batteries [1]. Electrochemical properties of the ZrO<sub>2</sub>-modified LiCoO<sub>2</sub> cathodes significantly change by modification methods and procedures that have been variously proposed [2]. The interactions between cathode surfaces and modification species during the modification might be crucial to determine the surface structures and the properties. However, there have been few surface modification techniques that can systematically control the interactions. Here we tried to control the interaction at the LiCoO<sub>2</sub> and ZrO<sub>2</sub> interface by changing the kinetic energy of ZrO<sub>2-x</sub> species during the modification using an arc plasma deposition (APD). APD can generate highly energetic evaporated species, and their kinetic energy when reaching the substrate can be controlled by the number of collisions with gasses in the chamber [3]. In this study, the surfaces of LiCoO<sub>2</sub> thin-film model electrodes were modified by amorphous ZrO<sub>2-x</sub> using APD under different O<sub>2</sub> pressures. The surface structures and electrochemical properties were investigated by X-ray photoemission spectroscopy (XPS) and charge-discharge measurements with cut-off voltages of 4.5 V and 2.8 V. The LiCoO<sub>2</sub> films were fabricated on Au substrates at room temperature by RF magnetron sputtering and were crystallized by post-annealing at 725 °C in O<sub>2</sub>. XRD and surface profiler analyses confirmed the formation of the 500 nm-thick polycrystalline LiCoO<sub>2</sub> films. Amorphous ZrO<sub>2-x</sub> lower than 1 nm was deposited on the LiCoO<sub>2</sub> surface by APD at different oxygen pressures of 30, 0.9 and 3 x 10<sup>-4</sup> Pa. The kinetic energy of ZrO<sub>2-x</sub> during the modification should decrease as the oxygen pressure increases. The film modified at 30 Pa showed the similar spectrum to the unmodified film. In contrast, the films modified at 0.9 and 3 x 10<sup>-4</sup> Pa showed that the chemical condition of the LiCoO<sub>2</sub> surface changed by the modification of ZrO<sub>x</sub> with relatively high kinetic energies. Charge-discharge tests clarified that the films modified under 0.9 and 3 x 10<sup>-4</sup> Pa exhibited high capacity retention of 70% and 68% at 125<sup>th</sup> cycle compared to the unmodified and the film modified under 30 Pa. The interaction between the ZrO<sub>2-x</sub> and the LiCoO<sub>2</sub> during the modification could play an important role in stabilizing the LiCoO<sub>2</sub> surface during the following electrochemical reactions. This work was partially supported by ALCA-SPRING of the Japan Science and Technology Agency.

## References:

- [1] D. Takamatsu, S. Mori, Y. Orikasa, T. Nakatsutsumi, Y. Koyama, H. Tanida, H. Arai, Y. Uchimoto and Z. Ogumi, *J. Electrochem. Soc.*, 2013, **160**, A3054-A3060.
- [2] G. T.-K. Fey, C.-Z. Lu, J.-D. Huang, T. P. Kumar and Y.-C. Chang, *J. Power Sources*, 2005, **146**, 65-70.
- [3] Y. Yamamoto *et al.*, *International Conference on Ion Implantation Technology Proceedings*, 1998, 1148.