HONEYCOMB ORDERING TO TRIGGER OXYGEN REDOX CHEMISTRY IN LAYERED CATHODE MATERIALS

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Even though Na_xMO_2 ($x \leq 1$, M = transition metal) materials have been studied for a long time as positive electrode candidates for Na-ion batteries, the available capacity is still limited. Partial substitution of M by Na^+ is an appealing strategy to overcome this issue: the excess Na^+ ions in the MO_2 layer could participate in the (de)intercalation process while lowering the weight of the battery, thus greatly enhancing the gravimetric capacity. This strategy, applied to Li-ion batteries for many years, is still poorly transferred to Na-ion battery materials.

In order to establish a model for the study of Na_2MO_3 materials, we prepared two polymorphs of O3-Na_2RuO_3[1,2], distinguished by the honeycomb-like ordering of the $[Ru_{2/3}Na_{1/3}]O_2$ layers. We identified that the ordered phase induces the spontaneous formation of an ilmenite-type intermediate which facilitates highly reversible oxygen redox chemistry associated to large extra capacity (Figure 1).

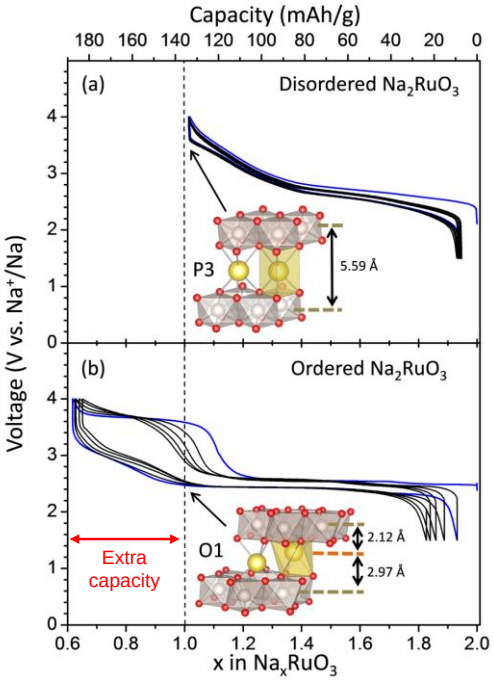

Figure 1. Galvanostatic cycling curves for (a) disordered and (b) ordered O3-Na_2RuO_3 (first cycle highlighted in blue). The insets represent the coordination environment of Na at x = 1.

[1] M. Tamaru, X. Wang, M. Okubo, A. Yamada, Electrochem. Comm. 33 (2013) 23 – 26.
[2] B. Mortemard de Boisse, G. Liu, J. Ma, S.-i. N, S.-C. Chung, H. Kiuchi, Y. Harada, J. Kikkawa, Y. Kobayashi, M. Okuboand A. Yamada, Submitted.