Migration of Mg in Na-O-Mg Configuration for Oxygen Redox of Sodium Cathode

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Mn-based P2-$Na_x[Li_yTM_{1-y}]O_2$ cathode materials are available to reach high capacity through the combination of cationic and anionic redox in Na cells.[1–11] The Na–O–Li configuration induces the delivery of additional capacity assisted by the oxidation of oxygen when lone-pair electrons are formed in the O 2*p* orbital, provided that at least one of the following conditions is satisfied: 1) lattice oxygen evolution[1] or 2) migration of the Li element to Na layers although the corresponding charge transfer is kinetically sluggish.[2] The reaction is not limited to compounds that have alkali ions in the TM layer but is also available with divalent ions; namely, the presence of Mg in the TM layer, P2-$Na_x[Mg_yMn_{1-y}]O_2$ (x = ~2/3, y = ~0.28).

The effect of the 4*d* Ru element in P2-$Na_{0.6}[Mg_{0.2}Ru_{0.2}Mn_{0.6}]O_2$ is investigated. Ru-free $Na_{0.6}[Mg_{0.2}Mn_{0.8}]O_2$ is activated with the Mn^{3+}/Mn^{4+} redox, after which the charge is compensated by the sluggish oxidation of lattice oxygen (O^{2-}) to O_2^{n-} triggered by O_2 evolution from the oxide lattice. These effects are generally unfavorable and result in poor long-term cycle stability induced by the irreversible migration of Mg^{2+} from the transition metal (TM) to Na layers in the P2 structural framework. Benefiting from the covalent Ru bonded with O in the TM layers, the Mg migration reversibly progresses from the TM to sodium slabs without O_2 evolution in the structure. The associated reaction progresses via the active Mn^{4+}/Mn^{3+} and $O^{2-}/(O_2)^{n-}$ reaction in addition to the $Ru^{5+}/Ru^{4+}/Ru^{3+}$ redox pairs, endorsing the capacity increase (~210 mAh g^{-1}), with ~72.1% retention for 300 cycles.

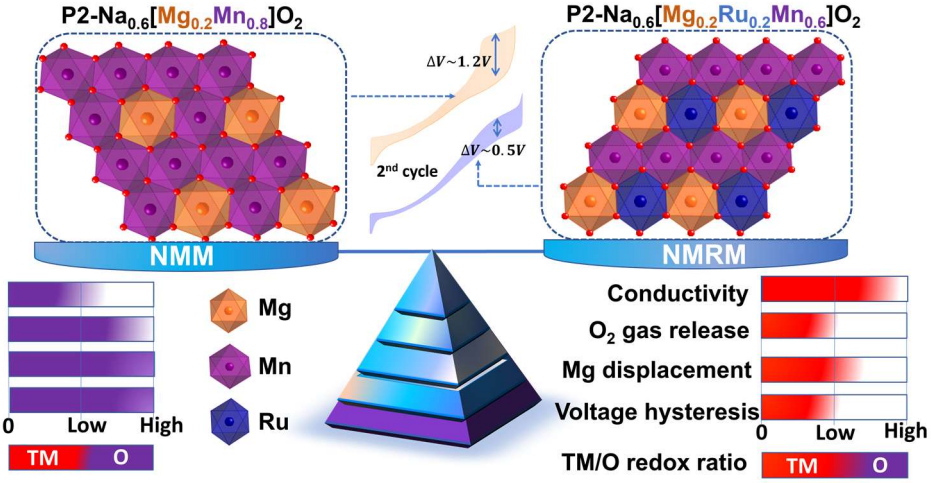

Figure 1. The presence of the higher-covalency Ru–O bond minimizes Mg migration from the TM to Na layers.

References

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