Supplementary information

A new lithium diffusion model in layered oxides based on asymmetric but reversible transition metal migration

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Supplementary figure 1

The first charge/discharge profiles of LNM244 operated at 25 °C and 60 °C are compared in Figure S1. Whereas 1.13 Li was extracted on 60 °C charge, only 0.79 Li was extracted on 25 °C charge. During the first charge of LNM244, Ni was oxidized from 3+ to 4+, and oxygen oxidation accompanied the rest of Li extraction. However, comparison of the Ni XANES peak change during the first charge reveals that Ni was fully oxidized at both temperatures (Figure S2a,b), indicating that the difference in the first charge capacity originates from the different amounts of oxygen oxidation. Therefore, LNM244 was pre-cycled at 60 °C and tested at 25 °C.



Supplementary figure 2.

Ni XANES spectra of LNM244 cycled at (a) 60 °C and (b) 25 °C. Although the Ni peak shifts in the full charged states are almost identical, a large difference in the discharged states is observed for the two temperatures. Comparison of the 2.0-V discharged states reveals that the cell operated at 60 °C was more reduced. (c) 60 °C charged and 25 °C 2.0-V discharged states (pink) are plotted together with Figure S2a. The plot is well fitted with the 3.5-V 60 °C discharged state, which indicates that it is not yet fully discharged, as shown in Figure 1a. (d) 60 °C 1 cycled and 25 °C charged state (green) are plotted together with Figure S2a. The plot is well fitted with the 60 °C full charged state, which indicates that the charge reaction at 25 °C is not inhibited, as shown in Figure 1b.



Supplementary figure 3. Electrochemical profile of LNM244 one cycled at 60 °C, followed by 25 °C charge and discharge. While there is a negligible reduction in the capacity at 25 °C during the charge reaction (step 2 to 3 and step 4 to 5), there is a clear reduction in the capacity during the discharge reaction (step 3 to 4).



Supplementary figure 4. GITT on 25 °C discharge with 250 mAh g⁻¹ cutoff and charge after 60 °C charge. 1-hour rest is applied between every constant current cycle. Clear asymmetric behavior between discharge and charge can be observed.



Supplementary figure 5. Electrochemical profile of LNM244 when it starts with discharge until 1.2 V from the pristine state.



pplementary figure 6. Comparison of 3 hours rest GITT (a), 1 hour rest GITT (b) operated at 25 °C.

Figure S6 presents that the effect of aging could be probed by comparing the discharge behaviors from the two pseudo GITT experiments, (i) one holding cells at OCVs for 3 hours (Figure S6a) and (ii) the other holding cells at OCVs for 1 hour (Figure S6b). When the cell was given with a shorter period of time in the rest step, the large polarization region appears at the comparatively earlier stage, indicating the more severe kinetic inhibition in this case. It is attributable to that the TM migration back to the TM layer could not take place sufficiently with the shorter rest time, thus a significant retardation of lithium diffusion appeared at this condition. On the other hand, if a sufficient rest time is given (*e.g.* 3 hours rest time), the partial redistribution between Li/TM could take place, which contributes to mitigating, to some extent, the kinetic hindrance with a delayed appearance of the large polarization region. It indicates that there is a clear driving force for TM/Li redistribution, where TM returns to the TM layer at low SOC, but it is much sluggish because of the distracted and extended migration path. And, once the sufficient resting time or kinetics is offered, it can be mitigated to some degree.



Supplementary figure 7. 25 °C discharge to 2.0 V (red), followed by transferring to 60 °C oven, rested and discharged (blue). It is compared with normal 60 °C discharge profile (black).

Supplementary note 1. LLO materials undergo structural changes involving the oxygen evolution and TM migration during the first charge, which have been observed from XRD (loss of superlattice peaks at 20-25°), TEM (TM migration to the lithium layer) and Raman spectroscopy.^{1,2} Yu *et al.* and Hy *et al.* observed a global Raman peak broadening of Li₂MnO₃ and Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ during the first charge, which is only partially reversible during the following discharge.^{3,4} Also, the peak broadening was more intensively observed during the electrochemical cycling of Li_{1.2}Ni_{0.2}Mn_{0.6}O₂.⁵ It indicates that a disappearance of peak at 548 cm⁻¹ after charge in figure 2g, which is assigned as the metal bonded to axial oxygen ligands, is due to the significant peak broadening arising from the structural evolution involving the oxygen release and TM migration during the first charge.



Supplementary figure 8. Discharge capacities coming from the low voltage plateau as a function of charge capacity. Inset shows the corresponding electrochemical profiles with identical charge and discharge capacities.

LNM244 is charged to various SOCs to investigate the charge capacity dependency of lithiation into the lithium tetrahedral site during following discharge. We varied charge capacity from 50 to 250 mAh/g, then discharged the same amount of charged capacity. In the figure, we plotted the discharge capacity that is delivered at the unusual low-voltage plateau (~ 2V) as a function of the charge capacity from 50 to 250 mAh/g, as the indicator for the TM migration/kinetic asymmetry. The plot displays that the low-voltage plateau capacity suddenly increases when the charge capacity gets higher than 150 mAh/g. And, when the charge capacity becomes 250 mAh/g (the highest SOC state), the low-voltage capacity gets the highest. When

comparing the increase in the low-voltage capacity from the first 100 mAh/g with that of the later 100 mAh/g, the latter presents nearly four times higher values, as indicated by the arrows in the figure. The sudden increase in the low-voltage discharge capacity starting from the certain high SOC implies that the TM migration gets appreciably promoted at sufficiently high SOC states. On the other hand, no significant change in the low-voltage discharge capacity was observed when the SOC of the electrode was below 150 mAh/g. It should be noted, nevertheless, that the low-voltage capacity is still observable even with the relatively low SOCs. It is attributable to (i) the inhomogeneity in the SOC states in the particle/electrode and (ii) the generally sluggish lithium diffusion in the layered materials at low SOC states.^{6,7} In the practical battery operation conditions, with the kinetic limitations within the particle and electrode, there exists unwanted reaction inhomogeneity in lithium de/lithiation. While the overall SOC appears to be low, certain part of the particle (e.g. shell region of the particle) or electrode can be locally higher in the SOC state than the overall value during charging, which may reach the condition of the TM migration. It would be more appreciable when the electrode suffers from the low kinetic properties. In recent years, this inhomogeneity in the particle and the electrode during charge or discharge has been directly probed using state-of-the-art spectroscopy tools such as scanning transmission X-ray microscopy.^{8,9}



Supplementary figure 9. DFT calculation results which show TM migration behaviors during charge and discharge. a, Possible trajectory of TM migration during the charging process. From the original position, TM ion can move to (i) tetrahedral site in the Li layer, (ii) octahedral site adjacent to i, (iii) tetrahedral site adjacent to ii, and (iv) octahedral site adjacent to iii, in turn. For a TM ion whose initial migration to the lithium layer (original \rightarrow 'i') is most thermodynamically favorable in the supercell, b and c present site energies calculated along the TM migration pathways. All possible sites to which TM ion can move at each step were considered, and the lowest site energy values are provided in the graph. One lithium layer and TM layers were fully delithiated during the calculation, so that it can describe highly charged state. To exclude the effects of slab space, it was fixed during the relaxation to be same with the value of b, the fully-lithiated state (2.63 Å), and c, the fully-delithiated state (2.92 Å), respectively. d and e represent the relative site energies calculated

along the returning migration path of TM ion ('iii' \rightarrow 'ii' \rightarrow 'i' \rightarrow original), starting from 'iii' site at which TM ion is predicted to arrive during charge. The site energies were estimated considering various lithium occupancies of the lithium layer in which TM ion is present (lithium occupancies are 0 ~ 0.167 for d, and 0.333~ 0.667 for e, respectively). Case I refers to the calculations with the fixed lithium slab space of 2.63 Å. Case II refers to those with the fixed lithium slab space of 2.92 Å. In e, the largest thermodynamic barrier required for each case are denoted. Note that when the lithium occupancy is higher than 0.667, TM occupation of tetrahedral site ('i') was prohibited, which is attributable to high instability of tetrahedral site sharing faces with more than three lithium ions.¹⁰



Supplementary figure 10. Electrochemical profiles of discharge and charge at 25 °C for various current densities after pre-cycle at 60 °C. a, Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O₂, b, Li_{1.2}Ni_{0.2}Mn_{0.6}O₂, c, Li₂Ru_{0.5}Sn_{0.5}O₃, d, LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂.

All of LLO materials show asymmetric charge/discharge kinetic behavior (a-c), while stoichiometric NCM811 show symmetric behavior (d). Also, it should be noted that the degree of asymmetry or the current density where asymmetric behavior appears are dependent on the composition of TM, such as ration of Ni/Mn or using Ru. It indicates that TM is a critical factor that affects asymmetric kinetic behavior between charge and discharge in LLOs. In the case of Ni, Co, Mn based lithium rich layered oxides in Figure 1a, S10a, S10b, while they all show

asymmetric charge/discharge behavior with sluggish discharge reaction, LNM244 exhibits the most distinct asymmetric behavior among them, implying the transition metal (TM) composition dependency. The possible reason for this is elaborated below.

When TM migration occurs toward the lithium layer during charge, the migrating TM can trigger the local formation of spinel-like phase especially for Mn-rich cases.⁵ According to the previous report, it accompanies with the reduction of Mn⁴⁺ to Mn³⁺, which prevails in most LLOs with high manganese contents, and it results in the simultaneous decrease in the operating voltage.¹¹ However, in the case of LLO with high nickel contents (LNM244), the nickel can act as a 'redox buffer', obstructing the reduction of Mn⁴⁺ and the formation of manganese-based spinel phase, as previously reported. In addition, due to the instability of LiNi₂O₄ spinel phase, migrated nickel in Li layer is not likely to form the spinel-like phase and rather acts as a defect disturbing the lithium diffusion.^{12,13} Considering these previous observations, we note that the asymmetric charge/discharge behavior of LLOs with high Mn contents is supposed to be, to some extent, mitigated by the local phase transitions to spinellike phases. Since the kinetic asymmetry arises from the TM migrations within the Li layer in the 'layered' framework, its effect in the spinel phase with three-dimensional ionic path would be lessened. On the other hand, LLO with Ni rich composition (LNM244) retains the pristine layered framework, as previously evidenced with the suppressed voltage decay, thus, the larger kinetic asymmetry is dominantly observed.

In the case of $Li_2Ru_{0.5}Sn_{0.5}O_3$ in Figure S10c, the asymmetric charge/discharge behavior is also similarly observed as to that of the LNM244 that retains layered framework. However, it appears at much higher current densities. We suppose that it is attributed to the intrinsically high electronic conductivity of Li_2RuO_3 -based compounds, which usually show high power capability.¹⁴ Generally enhanced transport kinetics of Li₂RuO₃-based compounds as compared with NCM materials would make the appreciable asymmetric kinetic behavior displayed only at high rates. Regarding the stoichiometric layered NCM materials in Figure S10d, the asymmetric charge/discharge behavior is much less intensively presented compared with the LLOs. It is attributable to that the presence of the Li in the TM layer in layered LLO material partly contributes to the asymmetric charge/discharge. TM migration within the Li layer would be influenced by the neighboring cations placed in TM layer during the hopping process. It has been well known that, in conventional layered transition metal oxides, the cation (*i.e.* Li ion) diffusion in the Li layer takes place through a hopping mechanism from one octahedral Li site to the other via tetrahedral site that face-shares with the cation in the TM layer. As it is believed that TM migration in the Li layer would follow the similar hopping mechanism, TM would have to hop through the tetrahedral site face-sharing with the cations in the TM layer. In the stoichiometric layered material such as NCM materials, the cations in the TM layer is always high-valent TM, thus the strong electrostatic interaction between the migrating TM and the TM ion occupying in TM layer would occur, which makes the TM migration in the Li layer energetically unfavorable. On the other hand, in the case of LLOs, some of the TM layer is occupied by the Li ions, thus there are cases where migrating TM can hop via the tetrahedral site face-sharing with Li ions. It will make the TM migration in the Li layer far more facile. Since the random TM migration in the Li layer is the root cause of the asymmetric charge/discharge behavior as described in the manuscript, the presence of Li ions in TM layer of LLOs is believed to have contributed to the pronounced TM migration, thus the asymmetric charge/discharge behavior. On the other hand, it is much mitigated within the stoichiometric layered transition metal oxides.

These distinct observations demonstrate that the composition of TM and the presence of Li in TM layer are critical factors in LLO, which governs the degree of charge/discharge asymmetry, where more understanding on the effect of various TM should be studied in our further work.

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