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# Origin of voltage decay in high-capacity layered oxide electrodes

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**Although Li-rich layered oxides ( $\text{Li}_{1+x}\text{Ni}_y\text{Co}_z\text{Mn}_{1-x-y}\text{O}_2$ ,  $> 250 \text{ mAh g}^{-1}$ ) are attractive electrode materials providing energy densities more than 15% higher than today's commercial Li-ion cells, they suffer from voltage decay on cycling. To elucidate the origin of this phenomenon, we employ chemical substitution in structurally related  $\text{Li}_2\text{RuO}_3$  compounds. Li-rich layered  $\text{Li}_2\text{Ru}_{1-y}\text{Ti}_y\text{O}_3$  phases with capacities of  $\sim 240 \text{ mAh g}^{-1}$  exhibit the characteristic voltage decay on cycling. A combination of transmission electron microscopy and X-ray photoelectron spectroscopy reveals that the migration of cations between metal layers and Li layers is a congenital feature of the charge-discharge process that increases the trapping of metal ions in interstitial tetrahedral sites. A correlation between these trapped ions and the voltage decay is established by expanding the study to both  $\text{Li}_2\text{Ru}_{1-y}\text{Sn}_y\text{O}_3$  and  $\text{Li}_2\text{RuO}_3$ ; the slowest decay occurs for the cations with the largest ionic radii. This effect is robust, and the finding provides insights into new chemistry to be explored for developing high-capacity layered electrodes that evade voltage decay.**

Lithium-ion battery technology, having the highest gravimetric and volumetric energy densities of commercialized batteries, has conquered the portable electronics market<sup>1,2</sup>. Moreover, it is the battery of choice for powering electric vehicles and has great potential for grid energy storage<sup>3</sup>. Success in these fields will depend on our ability to further increase their energy density<sup>4</sup> to ensure longer cruising autonomy for electric vehicle and lower cost (per kilowatt-hour) to compete with pumped hydroelectric storage for grid applications. To reach such targets, current research mainly focuses on the synthesis of new Fe-based poly-anionic compounds<sup>5,6</sup> and improving the layered oxides used at present<sup>7</sup>, the latter being the topic of this paper.

Layered oxides of general formula  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (NMC) exhibit the highest capacity ( $\approx 200 \text{ mAh g}^{-1}$ ) of any positive-electrode materials used at present<sup>8</sup>. The crystal structure of these materials can be considered as an ordered rock-salt derivative, where octahedrally coordinated Li and transition-metal cations ideally form alternating layers confined to the (111) planes of cubic oxygen close packing<sup>9</sup>. By modifying the chemical composition through substituting M with Li in the metal layers, Thackeray's and Dahn's groups have fabricated materials, termed as Li-rich layered oxides or Li-rich NMC ( $\text{Li}_{1+x}\text{Ni}_y\text{Co}_z\text{Mn}_{1-x-y-z}\text{O}_2$ ), exhibiting reversible capacities exceeding  $250 \text{ mAh g}^{-1}$  (refs 10,11). The extra capacity was recently shown by complementary X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) experiments to be nested in the contribution of reversible anionic ( $\text{O}^{2-} \rightarrow \text{O}_2^{2-}$ ) redox processes to the overall material capacity<sup>12,13</sup>. Nevertheless, it remains that these materials have poor electrode kinetics and undergo large voltage decays (that is, change in slope of the characteristic voltage-composition curves) on cycling, both

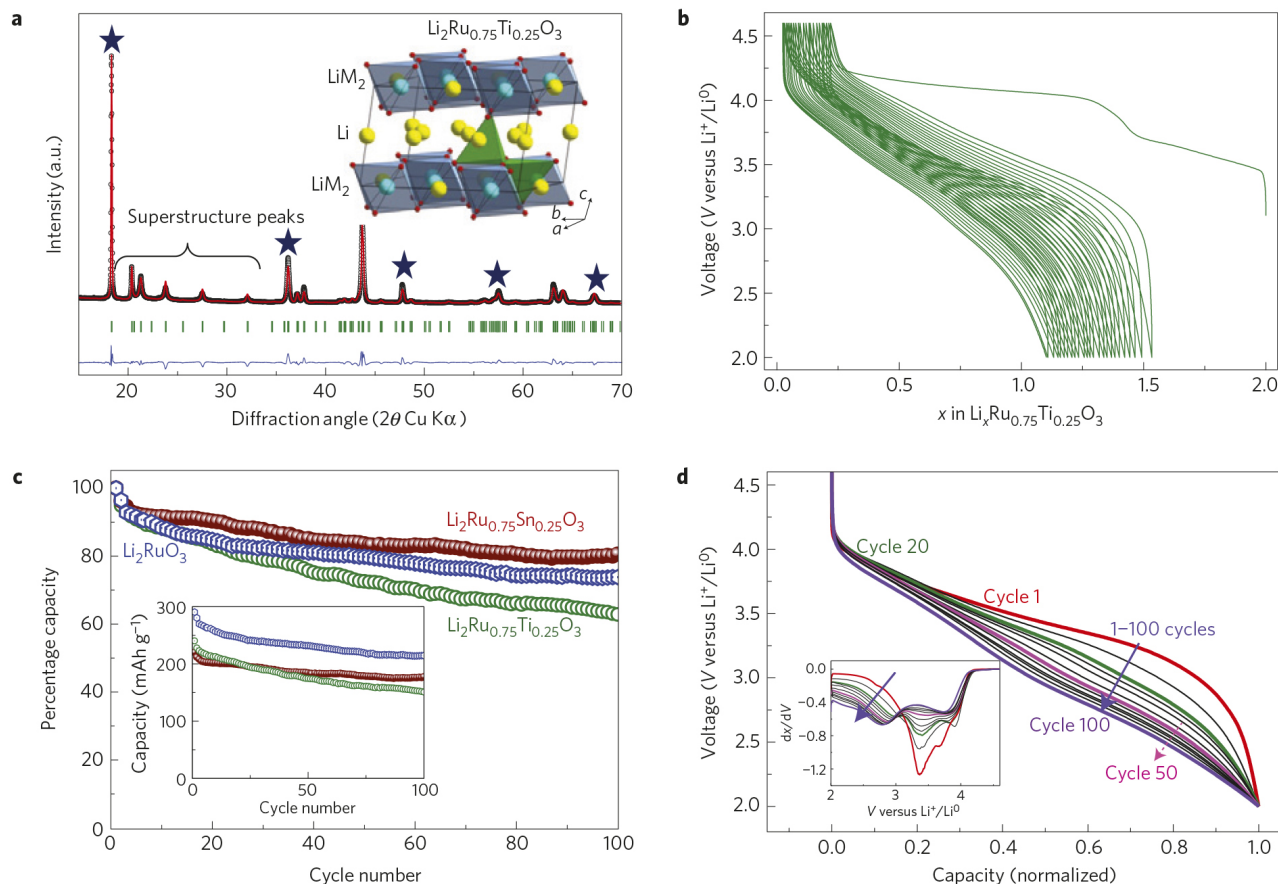
of which are plaguing their implementation in practical cells<sup>14-16</sup>. Present scenarios, although not fully conclusive, tend to relate this voltage decay to structural effects and more specifically to the formation of spinel-like domains<sup>17-23</sup>. We recently found that the replacement of  $\text{Mn}^{4+}$  in  $\text{Li}_2\text{Ru}_{1-y}\text{Mn}_y\text{O}_3$  by the larger and less electropositive cation  $\text{Sn}^{4+}$  reduces voltage fading<sup>12,24</sup>. To assess the importance of substituent's chemical-physical characteristics on the voltage fade on cycling, we herein extend our work to the study of  $\text{Li}_2\text{Ru}_{1-y}\text{Ti}_y\text{O}_3$ . The  $\text{Ti}^{4+}$  ( $d^0$ ) substitution was selected owing to its zero crystal field splitting, similar to  $d^{10} \text{Sn}^{4+}$ , its smaller size ( $0.60 \text{ \AA}$ ) and its presumed ability to show accelerated cation migration<sup>25,26</sup> for direct visualization of migration paths.

Members of the  $\text{Li}_2\text{Ru}_{1-y}\text{Ti}_y\text{O}_3$  series were prepared by thoroughly mixing stoichiometric amounts of  $\text{RuO}_2$ ,  $\text{TiO}_2$  and  $\text{Li}_2\text{CO}_3$  and annealing at  $800^\circ\text{C}$  for 24 h. The resulting single-phase samples form a complete solid solution, demonstrated by the continuous variation of lattice parameters as a function of Ti content (Supplementary Fig. 1). The crystal structure is monoclinic with an atomic distribution corresponding to the  $\text{Li}_2\text{RuO}_3$  model with some  $\text{Ru}^{4+}$  (ionic size  $0.62 \text{ \AA}$ ) being substituted by  $\text{Ti}^{4+}$  (ionic size  $0.60 \text{ \AA}$ ).

For concision, our study focuses mainly on  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$ . A combination of Rietveld refinement from powder X-ray diffraction (XRD) data (Fig. 1a), electron diffraction (Supplementary Fig. 2) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging (Supplementary Fig. 3) reveals that its structure can be viewed (Fig. 1a, inset) as stacking of  $\text{Li}_3$  layers and  $\text{LiM}_2$  layers ( $M = \text{Ru}, \text{Ti}$ ) along the  $c$  axis. In  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$ , the Li and (Ru, Ti) cations demonstrate perfect honeycomb-like ordering within the  $\text{LiM}_2$  layers; no cation inter-

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**Figure 1 | Structural and electrochemical aspects of  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$ .** **a**, Powder XRD pattern (black points) and the Rietveld fit (red lines) for  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$ ; refinement was carried out using the monoclinic  $C2/m$  space group (lattice parameters:  $a=5.037(7)$  Å,  $b=8.717(1)$  Å,  $c=5.126(6)$  Å and  $\beta=109.137(3)^\circ$ ). Bragg positions are indicated as green vertical tick marks, and the blue line is the difference between the observed and calculated patterns.  $R_{\text{Bragg}}=7.88\%$ . The peaks marked by stars are the reflections originating from the difference in scattering density between octahedral positions in the  $\text{Li}_3$  and  $\text{LiM}_2$  layers (interlayer ordering) and can serve as a mean to weigh the interlayer mixing, that is, the amount of transition-metal atoms (Ru/Ti) moving from the octahedral sites of the  $\text{LiM}_2$  layers (denoted  $\text{O}_{\text{LiM}_2}$ ) to the octahedral sites of the  $\text{Li}_3$  layers (denoted  $\text{O}_{\text{Li}_3}$ ). The inset shows the structure of  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  with stacking of  $\text{LiM}_2$  ( $M = \text{Ru}, \text{Ti}$ ) and  $\text{Li}_3$  layers; Li is yellow, Ru/Ti is blue, possible tetrahedral sites for the occupation of metal ions are shown by green (in the  $\text{Li}_3$  and  $\text{LiM}_2$  layer) tetrahedra. **b**, Voltage versus composition profile for  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  versus lithium as deduced from galvanostatic cycling at a 0.2 C rate. **c**, Percentage capacity retention plot of  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  in comparison with that of  $\text{Li}_2\text{RuO}_3$  and  $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$ ; the as-measured capacities are presented in the inset. **d**, From cycle 1 to 100, the galvanostatic discharge profile of  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  versus Li in the 2–4.6 V potential region; every tenth cycle is shown and the capacity values were normalized such that the maximum capacity in each cycle is taken as unity (240 and 151  $\text{mAh g}^{-1}$  is taken as unity for the first and hundredth cycles respectively). The inset shows the derivative plot of the same and the evolution of the new redox process at less than 3 V is marked by blue arrow.

1 mixing between the  $\text{Li}_3$  and  $\text{LiM}_2$  layers was observed. Thus, two  
 2 types of cation ordering coexist in the material. The interlayer  
 3 ordering between the  $\text{Li}_3$  and  $\text{LiM}_2$  layer drives the structure from the  
 4 cubic rock salt  $Fm\bar{3}m$  aristotype towards an  $R\bar{3}m$  sublattice, whereas  
 5 the honeycomb intralayer ordering decreases the symmetry even  
 6 further to monoclinic  $C2/m$ . Stacking faults are therefore abundant  
 7 (Supplementary Fig. 3) because of lateral shifts and/or  $60^\circ$  rotations  
 8 of the  $\text{LiM}_2$  layers.

9 The voltage–composition trace for a  $\text{Li}_2\text{Ru}_{1-y}\text{Ti}_y\text{O}_3$  electrode  
 10 ( $y=0.25$ ) shows the feasibility to remove 1.8 Li via two plateaus,  
 11 of which 1.5 Li can be reinserted via an S-type discharge curve  
 12 (Fig. 1b). This leads to a reversible capacity of nearly  $240 \text{ mAh g}^{-1}$   
 13 that decreases with increasing  $y$  and reaches  $110 \text{ mAh g}^{-1}$  for  
 14  $y=0.75$  (Supplementary Fig. 4).

15 A common feature of all members of the  $\text{Li}_2\text{Ru}_{1-y}\text{Ti}_y\text{O}_3$  solid  
 16 solution series is the large first-cycle irreversibility that increases  
 17 by increasing the cutoff potential (Supplementary Fig. 5). Such  
 18 irreversibility may occur partly owing to electrolyte oxidation but is  
 19 mainly caused by irreversible loss of oxygen from the material<sup>24,27,28</sup>  
 20 as confirmed by *in situ* gas and pressure analysis, with the onset of  
 21 an  $\text{O}_2$  loss at 4.1 V that then increases continuously as the charging

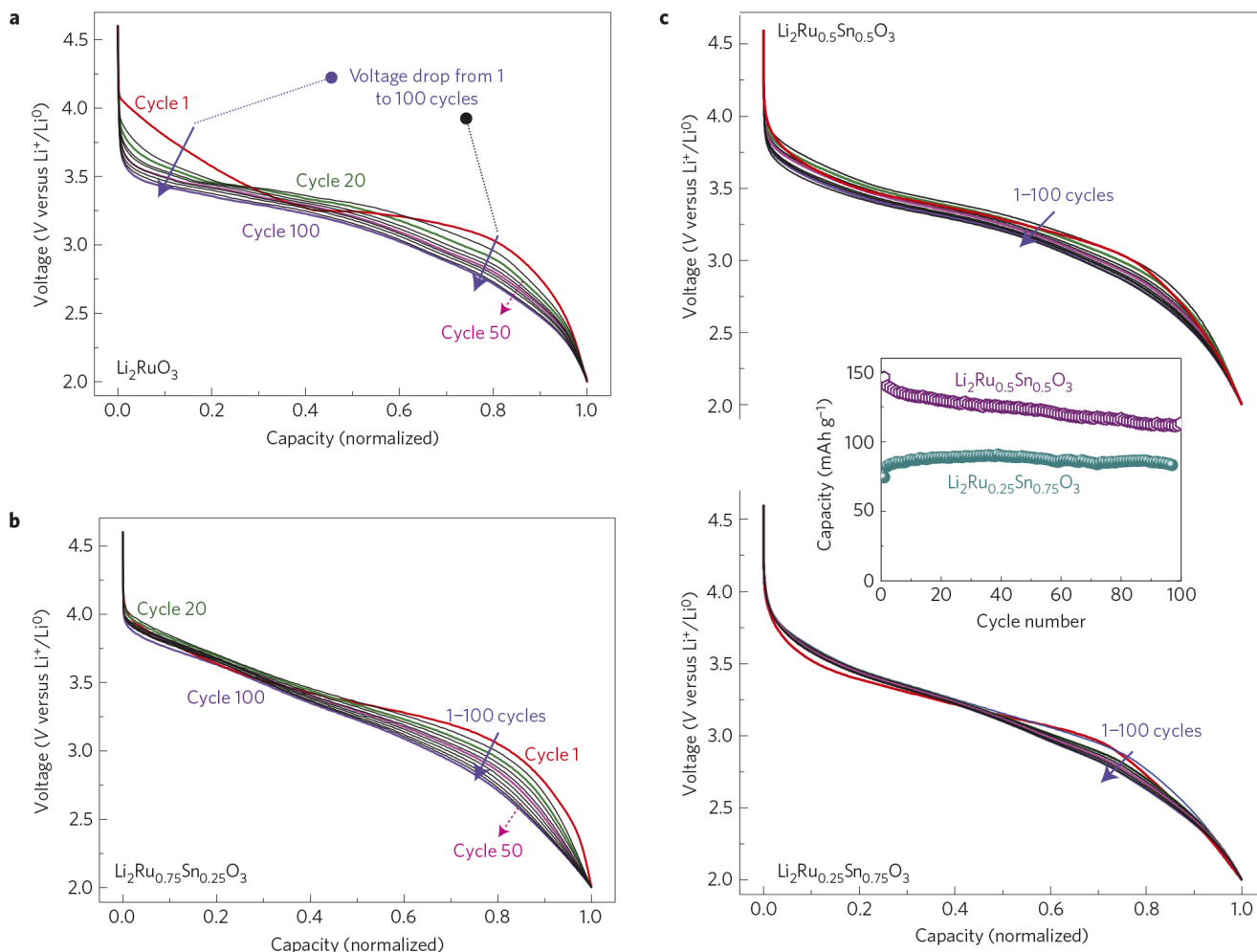
voltage proceeds to 4.5 V (not shown here). Last, similar to all Li-  
 rich NMC or  $\text{Li}_2\text{Ru}_{1-y}\text{M}_y\text{O}_3$  ( $M = \text{Mn}, \text{Sn}$ ) phases, the first charge  
 voltage trace differs from the first discharge trace, suggesting the  
 contribution of a reversible anionic ( $\text{O}^{2-} \rightarrow \text{O}_2^{2-}$ ) redox process to  
 the overall capacity of  $\text{Li}_2\text{Ru}_{1-y}\text{Ti}_y\text{O}_3$  samples. However, a minor  
 difference from the Mn- and Sn-based layered electrodes<sup>12,24</sup> is the  
 amplitude of the first-charge 3.7 V plateau for  $\text{Li}_2\text{Ru}_{1-y}\text{Ti}_y\text{O}_3$ , which  
 no longer equals the initial amount of Ru. This suggests another  
 redox process in competition with the  $\text{Ru}^{4+} \rightarrow \text{Ru}^{5+}$  process, as is  
 discussed later.

Long cycling tests performed on  $\text{Li}/\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  cells (Fig. 1c)  
 were compared to those of  $\text{Li}/\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$  and un-substituted  
 $\text{Li}_2\text{RuO}_3$  cells cycled under various cycling rates between 2 V and  
 4.6 V. All samples exhibit initial capacities exceeding  $200 \text{ mAh g}^{-1}$   
 (inset of Fig. 1c) with the Sn- and Ti-based samples showing the  
 highest and lowest capacity retention, respectively (90% versus 62%  
 after 100 cycles). This trend is preserved irrespective of the cycling  
 rate (data not shown here).

In addition, the normalized discharge voltage traces for a  
 $\text{Li}/\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  cell show that the voltage decays by nearly  
 500 mV between the first and hundredth cycle (Fig. 1d). This voltage

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**Figure 2 | Cycling behaviour of  $\text{Li}_2\text{Ru}_{(1-y)}\text{M}_y\text{O}_3$  ( $\text{M} = \text{Ru}/\text{Sn}/\text{Ti}$ ) in the view towards voltage decay. a–c**, Normalized capacity discharge profiles for  $\text{Li}_2\text{RuO}_3$  (a),  $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$  (b),  $\text{Li}_2\text{Ru}_{0.5}\text{Sn}_{0.5}\text{O}_3$  and  $\text{Li}_2\text{Ru}_{0.25}\text{Sn}_{0.75}\text{O}_3$  (c) from 1 to 100 cycles; the data are reported only for every 10 cycle. The capacity retention for  $\text{Li}_2\text{Ru}_{0.5}\text{Sn}_{0.5}\text{O}_3$  and  $\text{Li}_2\text{Ru}_{0.25}\text{Sn}_{0.75}\text{O}_3$  samples is shown as an inset in c. The capacity normalization was performed by taking the maximum discharge capacity in the corresponding cycle as unity.

1 decay occurs mainly over the low potential region as confirmed by  
 2 derivative curves (Fig. 1d inset), which show a progressive dumping  
 3 of high to low voltage peak. When comparing the different M-  
 4 based ( $\text{M} = \text{Ti}, \text{Sn}, \text{Ru}$ ) samples, the voltage decay on cycling mirrors  
 5 the capacity decay and is the smallest ( $\sim 150$  mV after 100 cycles)  
 6 for  $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$  (Fig. 2b). Such a trend persists whatever the  
 7 amount of substituent ( $y$ ; Supplementary Fig. 6). Note that the  
 8 voltage decay is gradually reduced with increasing amounts of Sn in  
 9  $\text{Li}_2\text{Ru}_{1-y}\text{Sn}_y\text{O}_3$  (Fig. 2a–c) with almost no voltage fading observed  
 10 after 100 cycles and nearly 100% capacity retention for  $y = 0.75$   
 11 (Fig. 2c inset). This clearly confirms the positive role played by larger  
 12  $\text{Sn}^{4+}$  ions in reducing the voltage decay over many cycles.

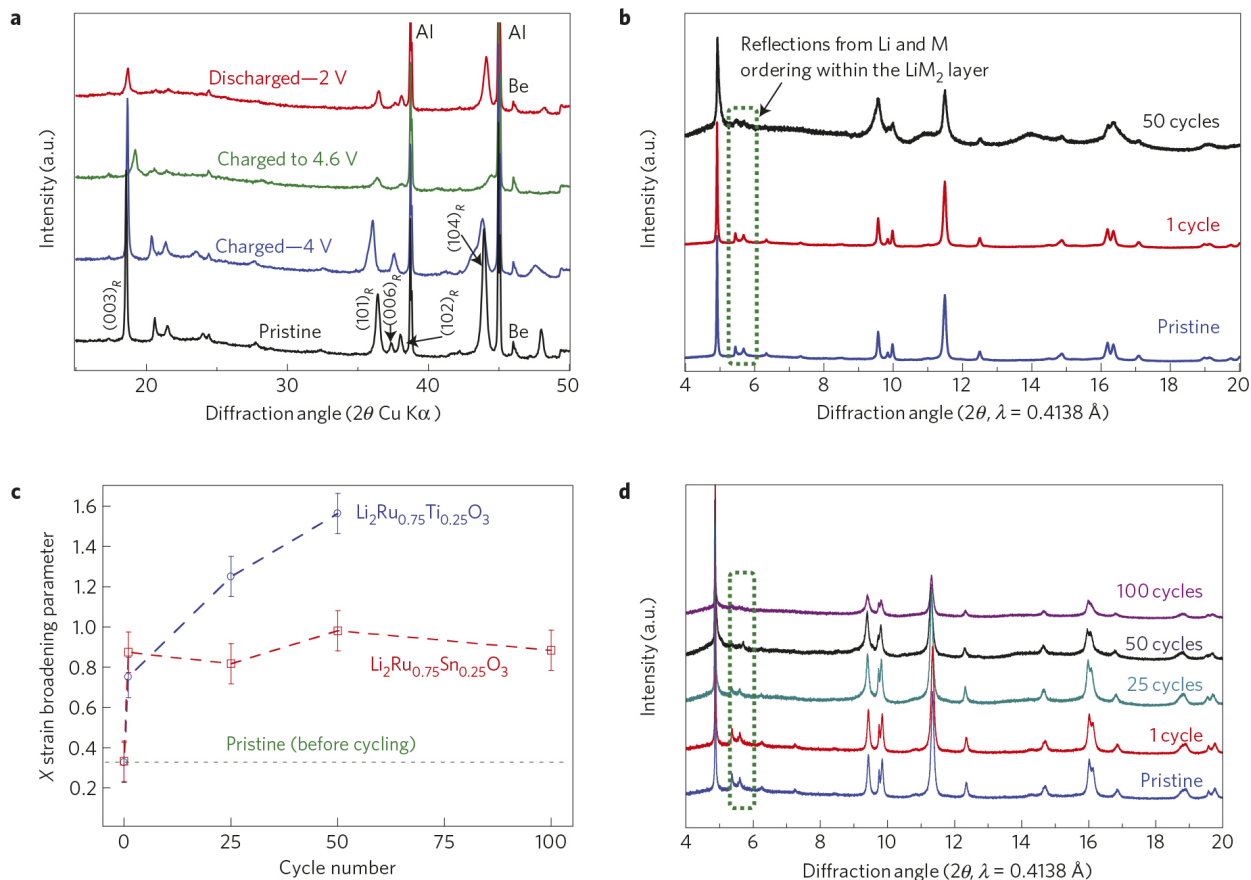
13 Cycling tests were also done as a function of charge cutoff voltage  
 14 (Supplementary Figs 7 and 8). When cycling is limited to the  
 15  $\text{Ru}^{4+}/\text{Ru}^{5+}$  redox couple ( $< 4$  V) 100% capacity retention is observed  
 16 for all systems, whereas the associated voltage decays vary from  
 17 nearly zero for Sn to 80 mV for Ti. This suggests that capacity  
 18 and voltage decay are not systematically related, as it may appear  
 19 by raising the charge cutoff voltage to 4.2 V and 4.6 V where we  
 20 note that both the capacity and voltage decay decrease in a similar  
 21 manner on cycling.

22 *In situ* XRD patterns were collected at different states of  
 23 charge/discharge for the  $\text{Li}/\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  cell cycled at C/20 rate  
 24 (Fig. 3a). As the cell is being charged to 4 V, an anisotropic variation  
 25 of the lattice parameters is observed with  $c/a$  ratio decreasing from  
 26 4.99 to 4.92 suggesting a gradual suppression of  $\text{Li}_3$ – $\text{LiM}_2$  interlayer

ordering. When further charging the cell to 4.6 V, many Bragg peaks  
 27 broaden and experience changes in relative intensities, indicative of  
 28 a possible migration of Ru/Ti from  $\text{LiM}_2$  to  $\text{Li}_3$  layers. On subsequent  
 29 discharge, the structure nearly converts back to the pristine layered  
 30 ordered structure with however an increasing cation disorder within  
 31 the  $\text{LiM}_2$  layers as deduced from the reduction in intensity of  
 32 superstructure peaks arising from the honeycomb  $\text{LiM}_2$  pattern.  
 33

34 To assess structural changes on prolonged cycling, high-  
 35 resolution synchrotron powder diffraction patterns were collected  
 36 for the pristine  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  and for electrodes recovered in  
 37 the discharged state after 1 and 50 cycles, respectively (Fig. 3b).  
 38 After 50 cycles, the XRD pattern significantly differs from that  
 39 of the first cycle by an intense peak broadening and a  
 40 progressive disappearance of the superstructure peaks. Owing to  
 41 such broadening, the patterns were refined in the  $R\bar{3}m$  subcell  
 42 using an  $X^* \tan \theta$  dependence accounting for strain effects; we  
 43 observed a sharp increase of the strain broadening parameter  $X$  with  
 44 increasing cycle numbers (Fig. 3c). Interestingly, the XRD pattern  
 45 of the  $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$  electrode cycled in similar conditions (C/10  
 46 rate, cycle numbers 1, 20, 50 and 100) shows a constant  $X$  parameter  
 47 (Fig. 3d), suggesting a correlation between the voltage decay and  
 48 micro-strains induced by local disorder (cation migration and/or  
 49 stacking fault).

50 XPS analyses were carried out on pristine  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$   
 51 (Fig. 4a) and on similar electrodes charged to  $\sim 3.9$  V (Fig. 4b)  
 52 and 4.6 V (Fig. 4c), and charge discharged to 2 V (Fig. 4d). The



**Figure 3 | Li-driven structural changes of  $\text{Li}_2\text{Ru}_{0.75}\text{M}_{0.25}\text{O}_3$  ( $\text{M} = \text{Sn/Ti}$ ).** **a**, *In situ* XRD pattern of  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  versus Li cells; the patterns collected on pristine electrode, during charge at 4 V, 4.6 V and then on completely discharged sample (2 V). On charging the  $\text{Li}/\text{Li}_{1-x}\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  cell to 4 V, there is a shift in the  $(003)_R$  peak towards higher  $2\theta$  and merging of  $(006)_R$  and  $(102)_R$  Bragg peaks (indexed in  $R\bar{3}m$ ) indicating an anisotropic variation of lattice parameters with the removal of lithium. On discharge, most of the peaks regained their intensity and reappearance of  $(006)_R$  and  $(102)_R$  peak splitting shows that the structure converts back to the pristine layered ordered structure. **b**, Synchrotron powder XRD pattern of pristine  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  and samples collected at the discharged state (2 V) after 1 cycle and 50 cycles. **c**, Variation of the Lorentzian broadening parameter  $X^* \tan\theta$  with cycling derived from refinement of the synchrotron XRD patterns. **d**, Synchrotron powder XRD pattern of pristine  $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$  and samples cycled several times (1, 25, 50 and 100 cycles) between 4.6 and 2 V and collected at 2 V. The green region in **b** and **c** shows the reflections from honeycomb Li-M ordering within the  $\text{LiM}_2$  layers.

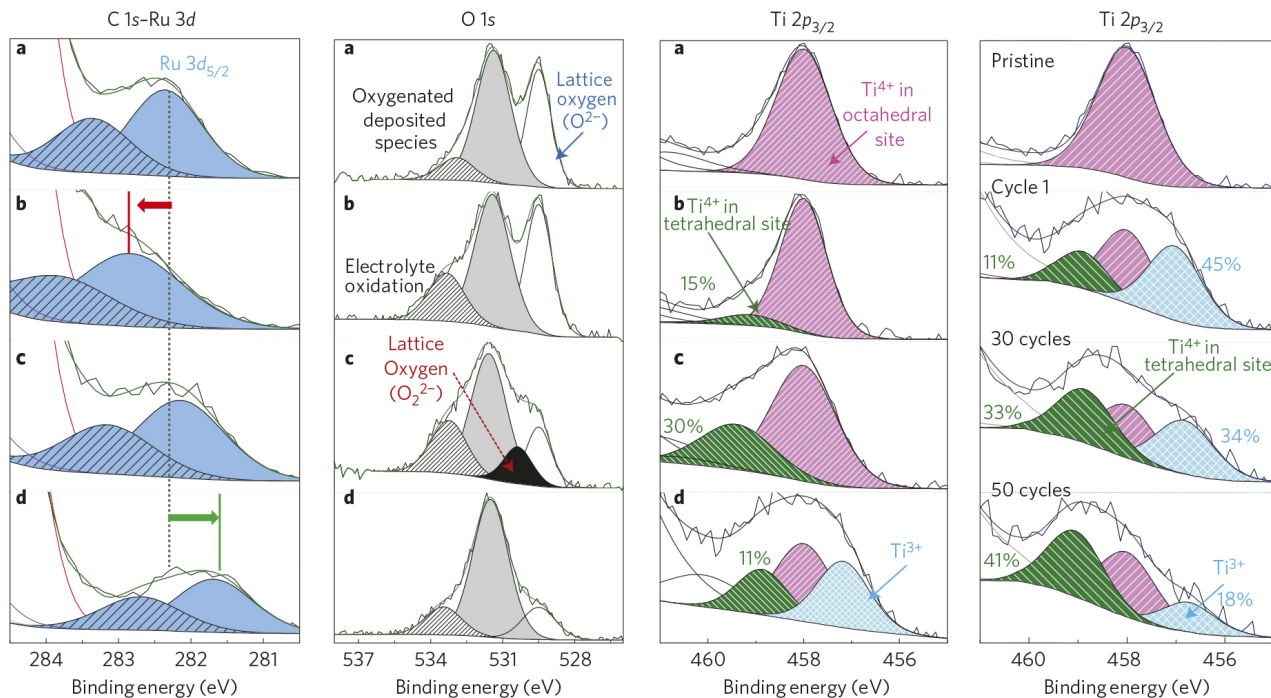
1 evolution of Ru  $3d_{5/2}$  and O  $1s$  core spectra along charge/discharge  
 2 is very similar to what was previously observed in Sn-based  
 3 electrodes<sup>22</sup>. The shift to higher binding energy of the Ru  $3d_{5/2}$   
 4 core peak on moving from OCV to 4 V identifies the  $\text{Ru}^{4+} \rightarrow \text{Ru}^{5+}$   
 5 oxidation process<sup>29</sup> (Fig. 4, left), while the appearance of the  
 6 530.4-eV O  $1s$  component at higher voltages is characteristic  
 7 of the formation of peroxo-like  $\text{O}_2^{2-}$  species<sup>30</sup>. A peculiarity  
 8 here is the appearance of an  $\text{O}_2^{2-}$  peak in the 4 V sample  
 9 before complete oxidation of  $\text{Ru}^{4+} \rightarrow \text{Ru}^{5+}$ , for reasons to be  
 10 discussed later (Supplementary Fig. 9). Repeated discharge-charge  
 11 (Supplementary Fig. 10) demonstrates the reversibility of these  
 12  $\text{Ru}^{4+} \rightleftharpoons \text{Ru}^{5+}$  and  $\text{O}^{2-}/\text{O}_2^{2-}$  processes, the latter being also  
 13 confirmed by parallel EPR measurements (Supplementary Fig. 11)  
 14 as previously described for the  $\text{Li}_2\text{Ru}_{1-y}\text{Sn}_y\text{O}_3$  phases<sup>12</sup>.

15 The true novelty here comes from the evolution of Ti  $2p_{3/2}$   
 16 core spectra. In the pristine electrode, the Ti  $2p_{3/2}$  component  
 17 observed at 458.0 eV and the binding energy difference (O  $1s$ -Ti  
 18  $2p_{3/2}$ ) of 71.5 eV are characteristic of  $\text{Ti}^{4+}$  ions in an octahedral  
 19 environment<sup>31</sup>. For samples charged to 3.9 V a small shoulder  
 20 appears at 459.1 eV, which becomes prominent at 4.6 V. Such  
 21 a high binding energy (that is, decrease in electron density) is  
 22 characteristic of  $\text{Ti}^{4+}$  in a tetrahedral environment as reported  
 23 earlier<sup>32</sup> and can be explained by weaker Ti  $3d$ -O  $2p$  overlap  
 24 in the tetrahedral environment. The amount of tetrahedral  $\text{Ti}^{4+}$ ,  
 25 as deduced from integration of the spectra, is  $\sim 15\%$  and  $\sim 30\%$

for the 3.9 V and 4.6 V samples, respectively. This result is  
 consistent with the relative ease of  $\text{Ti}^{4+}$  ions migrating from  
 octahedral to tetrahedral coordination due to the absence of ligand  
 field stabilization<sup>25,33</sup>. At this point, it is tempting to suspect a  
 correlation between the formation of  $\text{O}_2^{2-}$  entities and the  $\text{Ti}^{4+}$   
 migration, but such a correlation cannot be ascertained owing to  
 the large contamination by surface oxide species that render the  
 spectral deconvolution speculative given the small amount of  
 $\text{O}_2^{2-}$ . After discharge, there is appearance of an additional  
 component at 457.2 eV which can be attributed to  $\text{Ti}^{3+}$  ions  
 (reduction of  $\text{Ti}^{4+}$ ). From quantitative analysis we could deduce  
 that the amount of  $\text{Ti}^{3+}$  is about 35% and that octahedral  $\text{Ti}^{4+}$   
 ions are mainly involved in the reduction process. The spectra  
 obtained after 30 and 50 cycles clearly indicate an increase in  
 the amount of tetrahedral titanium from  $\sim 25\%$  after the first  
 cycle to  $\sim 40\%$  after 50 cycles. Those values are further refined  
 by the investigation of Ti  $3p$  core peaks (Supplementary Fig. 12),  
 which offer less surface sensitivity, indicating a similar evolution  
 over many cycles with slightly lower amounts of titanium in  
 tetrahedral sites (1 cycle:  $\sim 20\%$ , 50 cycles:  $\sim 34\%$ ). Unfortunately,  
 a similar approach is not feasible with Ru  $3d$  because of the  
 less resolved core spectra associated with the  $\text{Ru}^{4+} \rightarrow \text{Ru}^{5+}$   
 oxidation process. Last, the invariance of Sn  $3d$  core spectra when  
 charging/discharging  $\text{Li}_2\text{Ru}_{1-y}\text{Sn}_y\text{O}_3$  implies the absence of  $\text{Sn}^{4+}$   
 migration to tetrahedral interstices<sup>12</sup>.

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**Figure 4 | XPS of  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$ .** a-d, XPS spectra of the pristine  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  sample (a), 3.9 V (b), sample charged to 4.6 V (c) and charge discharged to 2 V (d). C 1s-Ru 3d spectra showing the Ru 3d<sub>5/2</sub> peak (blue region) together with a satellite peak (dashed blue region). The red and green arrows and lines are guides to the eye to show the shifting of the Ru 3d<sub>5/2</sub> peak with charging and discharging. The O 1s core spectrum consists of two peaks corresponding to crystalline O<sup>2-</sup> (529.5 eV) and surface oxidized species (531.6 eV). The new component appearing at 530.5 eV for the sample charged to 4.6 V is due to peroxy-like species associated with anion contribution for the redox process. Ti 2p<sub>3/2</sub> spectra, as a function of the cell voltage, are shown in the second panel from the right to highlight the partial migration of Ti<sup>4+</sup> from the octahedral site together with its partial reduction on discharge. The right panel shows the evolution of the Ti 2p<sub>3/2</sub> spectra with increasing number of cycles (1, 30 and 50 cycles).

Overall, XPS results show: that the Li-uptake/removal process in  $\text{Li}_2\text{Ru}_{1-y}\text{Ti}_y\text{O}_3$  involves cumulative contributions of cationic ( $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}/\text{Ru}^{5+} \rightarrow \text{Ru}^{4+}$ ) and anionic ( $\text{O}_2^{2-} \rightarrow \text{O}^{2-}$ ) reversible redox processes; and a significant amount of  $\text{Ti}^{4+}$  migration from octahedral to tetrahedral interstices that increases on cycling (Fig. 4, right). To address the preferentially reduced  $\text{Ti}^{4+}$  sites, EPR was performed on the  $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$  electrode, discharged to 2 V. The 4.2 K EPR spectrum (Supplementary Fig. 11) shows a set of two signals, with a weak *g* anisotropy (*g* = 1.92 and 1.89) for the first one and a lower *g* factor (1.79) for the second, which we ascribe to octahedral and tetrahedral  $\text{Ti}^{3+}$  centres, respectively<sup>34,35</sup>. This result confirms the  $\text{Ti}^{4+}/\text{Ti}^{3+}$  reduction process detected by XPS, and provides evidence for the feasibility to partially reduce  $\text{Ti}^{4+}$  in both tetrahedral and octahedral sites, although quantification could not be done.

Another feature that cannot be deduced by XPS is the degree of cation migration between octahedral sites within the  $\text{LiM}_2$  layers and the  $\text{Li}_3$  layers, hereafter denoted as  $\text{Oc}_M$  and  $\text{Oc}_{\text{Li}}$ , respectively, owing to nearly identical binding energies of both environments. The most natural technique to visualize cation migration at the local scale is HAADF-STEM. Thus, HAADF-STEM images were collected for the  $\text{Li}_2\text{Ru}_{0.75}\text{M}_{0.25}\text{O}_3$  (*M* = Ti, Sn, Ru) electrodes cycled in similar conditions for various states of charge and discharge. Details on interpretation of the HAADF-STEM images are provided in Supplementary Figs 13 and 14.

We first studied the pristine  $\text{Li}_2\text{Ru}_{0.75}\text{M}_{0.25}\text{O}_3$  material for which HAADF-STEM images revealed a two-dimensionally ordered structure with perfect Li and (Ru, Ti) ordering within the  $\text{LiM}_2$  layers and no antisite defects between the  $\text{Li}_3$  and  $\text{LiM}_2$  layers (Supplementary Fig. 3). This contrasts with the overview [100] HAADF-STEM image (Fig. 5a) collected for a fully charged sample that shows the removal of Li to cause massive micro-structural changes, specifically: substantial disorder of the Li and (Ru, Ti) cations within the  $\text{LiM}_2$  layers; migration of significant fractions of

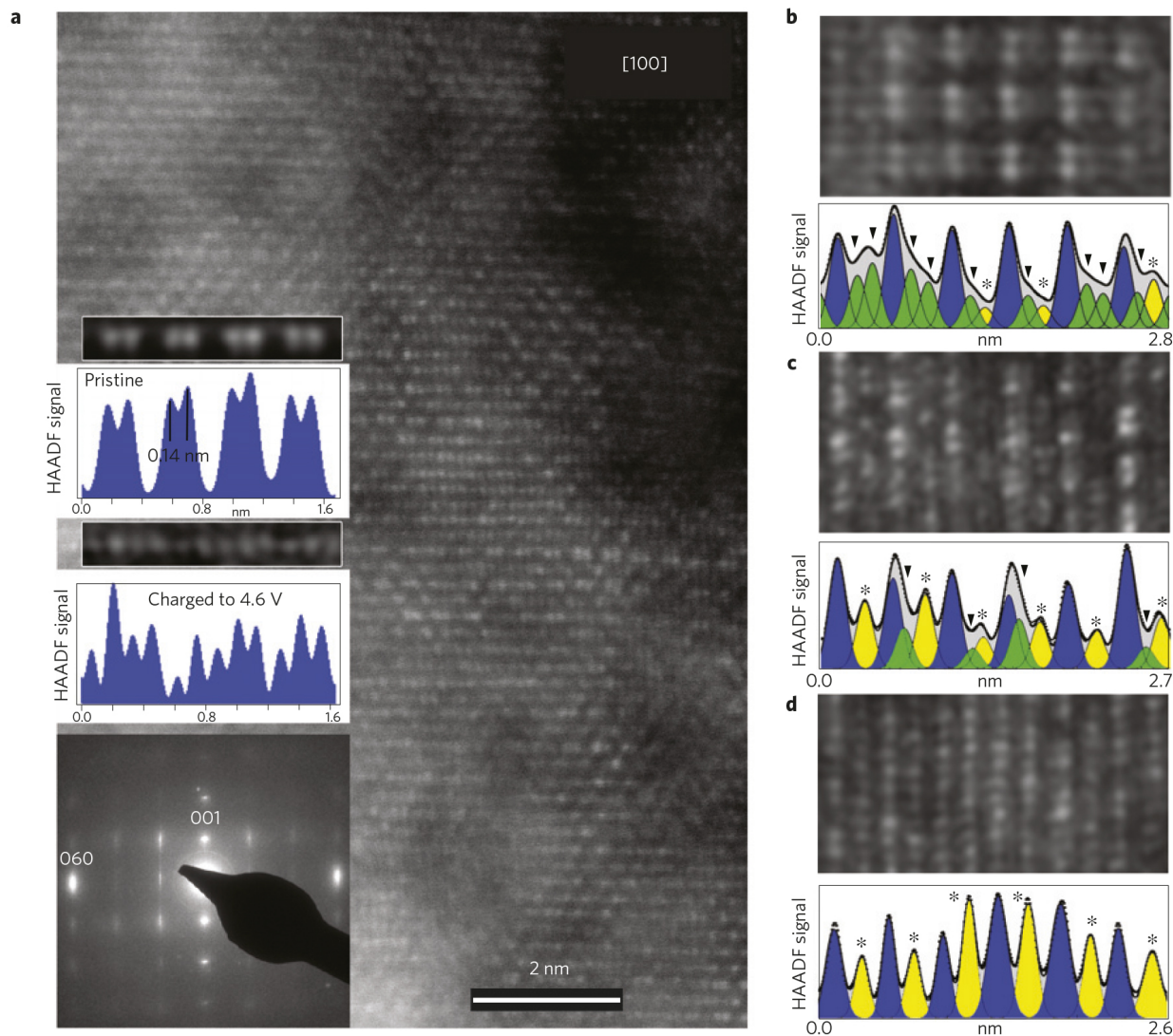
(Ru, Ti) cations from the octahedral  $\text{Oc}_M$  positions in the  $\text{LiM}_2$  layers to the octahedral positions  $\text{Oc}_{\text{Li}}$  in the  $\text{Li}_3$  layers; and the presence of local areas with partial occupation of the tetrahedral interstices between the  $\text{LiM}_2$  and  $\text{Li}_3$  layers by the (Ru, Ti) cations. These structural changes are not homogeneous throughout the sample, as highlighted by the three typical HAADF-STEM images in Fig. 5b-d. In the portion of the sample probed in Fig. 5b, Li and (Ru, Ti) ordering within the  $\text{LiM}_2$  layers is mainly preserved, but a fraction of (Ru, Ti) cations migrate to the tetrahedral interstices and a marginal amount of cations move to the  $\text{Oc}_{\text{Li}}$  positions. In the area shown in Fig. 5c, the occupation of  $\text{Oc}_{\text{Li}}$  positions is greater, with nevertheless some (Ru, Ti) cations remaining at tetrahedral interstices. Last, the image in Fig. 5d shows a part of the sample in which a large fraction of (Ru, Ti) cations have moved to the  $\text{Oc}_{\text{Li}}$  site and virtually no M cations remain in the tetrahedral sites.

Turning to the discharged  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  sample (Supplementary Fig. 15), the HAADF-STEM pattern nearly converges back to that of a pristine sample, implying that most of the cations migrate back to their initial positions. Nevertheless, some remaining traces of cations in tetrahedral interstices are observable at the edge of the crystallite, and also at the distances of 15–25 nm towards the crystallite core, where the image resolution is not yet deteriorated markedly by increasing the crystal thickness (Supplementary Fig. 16).

Next, we collected HAADF-STEM images of a  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  electrode cycled 50 times. The images significantly differ from those collected after one cycle, showing an intense disorder of Li and (Ru, Ti) cations within the  $\text{LiM}_2$  layers and migration of (Ru/Ti) atoms away from the  $\text{LiM}_2$  planes towards neighbouring interstitial positions (Fig. 6a,c, left). Fitting of the HAADF-STEM signal profile reveals a dominance of peaks corresponding to the migration of (Ru/Ti) cations towards tetrahedral sites, with peaks reminiscent of  $\text{Oc}_{\text{Li}}$  site occupancy being barely visible. Overall it clearly indicates, in agreement with XPS results, that the occupancy of interstitial

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**Figure 5 | HAADF-STEM images of  $\text{Li}_{2-x}\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  electrodes.** **a**, [100] overview HAADF-STEM image of the  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  sample charged to 4.6 V. The insets show (from top to bottom): HAADF-STEM image of the atomic columns in the  $\text{LiM}_2$  layer of the pristine  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  sample along with the corresponding intensity profile demonstrating pair of dots separated by  $\sim 0.14$  nm (this corresponds to perfect honeycomb ordering of the Li and M cations within the  $\text{LiM}_2$  layers); HAADF-STEM image of the atomic columns in the  $\text{LiM}_2$  layer of the charged  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  sample along with the corresponding intensity profile demonstrating significant disorder of the M cations within the  $\text{LiM}_2$  layers; selected-area electron diffraction pattern of the charged  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  sample showing lines of diffuse modulated intensity at the  $k \neq 3n$  positions due to local remaining order of the M cations in the  $\text{LiM}_2$  layers. **b-d**, Images and corresponding HAADF-STEM signal profiles illustrating the different stages of the cation migration. **b**, The pristine structure is mostly preserved, most of the (Ru, Ti) cations are in the octahedral  $\text{Oc}_{\text{LiM}_2}$  positions (blue peaks on the profiles), but a fraction of the (Ru, Ti) cations are moved to the tetrahedral interstices (green peaks on the profile marked with arrowheads). Occupation of the octahedral positions in the  $\text{Li}_3$  layer remains marginal (yellow peaks on the profile marked with asterisks). **c**, Occupation of the octahedral positions in the  $\text{Li}_3$  layer increases, some (Ru, Ti) cations remain at tetrahedral interstices. **d**, A large fraction of the (Ru, Ti) cations are moved to the octahedral position in the  $\text{Li}_3$  layer. For simplification, in the aforementioned description, the  $\text{Li}_3$  and  $\text{LiM}_2$  layers of the pristine structure are termed as  $\text{Li}_3$  and  $\text{LiM}_2$  although the cation composition of these layers is changed substantially owing to cation migration.

tetrahedral sites increases with the number of cycles. A simple explanation is that the cations are progressively trapped within the tetrahedral sites as they migrate back and forth between  $\text{Oc}_M$  and  $\text{Oc}_{\text{Li}}$  sites, suggesting a possible correlation between the voltage decay and the trapping degree on cycling.

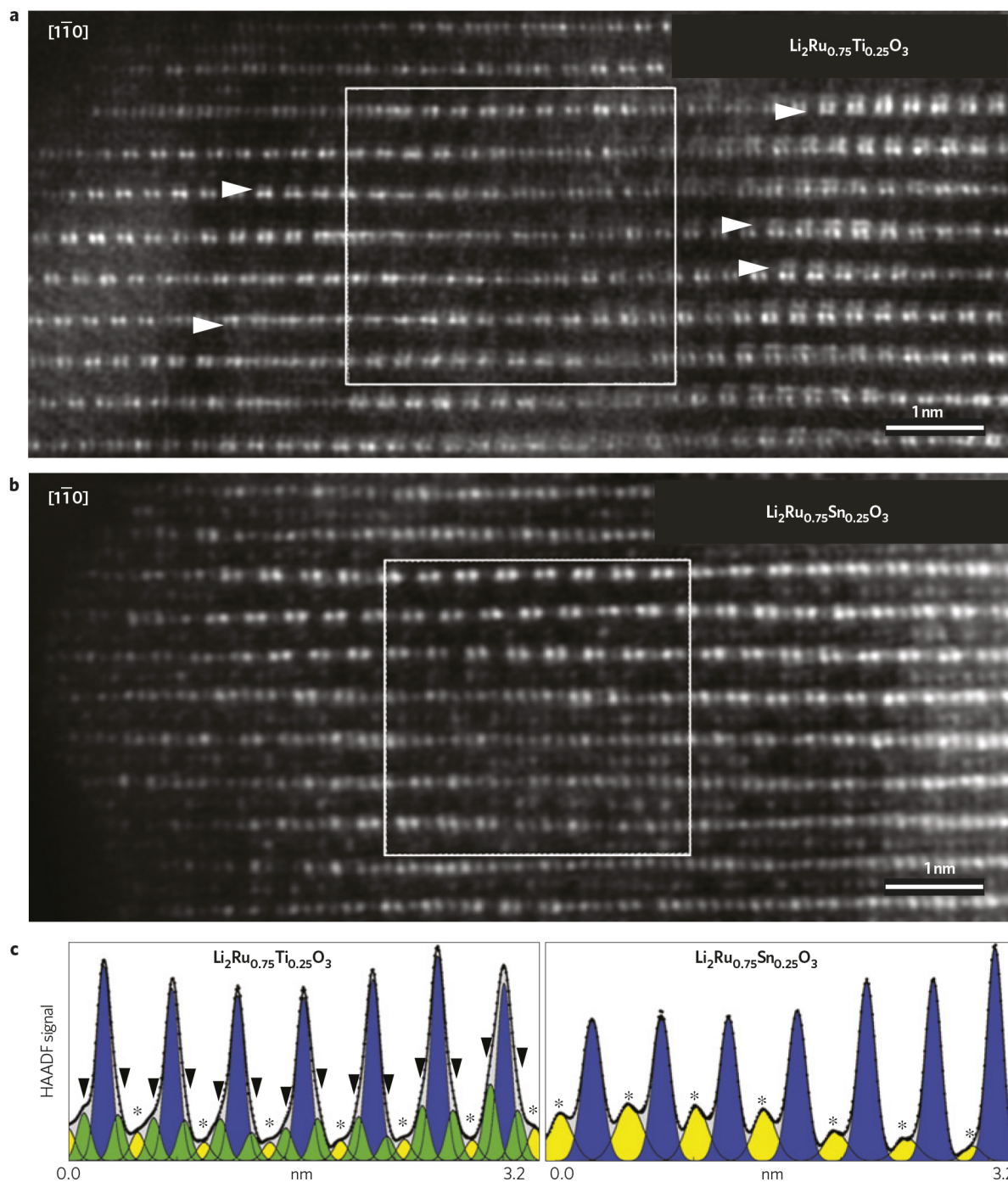
To test such a possible correlation we explored  $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$  (Fig. 6) electrodes that had been cycled 100 times and showed the lowest voltage decay. HAADF-STEM images provide direct evidence for cation migration towards  $\text{Oc}_{\text{Li}}$  sites in this system as well (Fig. 6b,c, right). More important is the quasi absence of cations in tetrahedral sites for this sample, further supporting our tentative correlation.

Finally, to clarify the outcome of Ru ions on cycling, we also studied  $\text{Li}_2\text{RuO}_3$  electrodes cycled once, and after 100 cycles (Supplementary Figs 17 and 18). Comparing the HAADF-STEM

image of  $\text{Li}_2\text{RuO}_3$  and  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  electrodes after one charge-discharge cycle (Supplementary Figs 16 and 17) reveals virtually no population of tetrahedral sites in the pure Ru sample. This contrasts with the HAADF-STEM images collected after 100 cycles, which indicate the presence of Ru in tetrahedral sites. However, a comparison of the HAADF-STEM signal profiles of  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  and  $\text{Li}_2\text{RuO}_3$  samples cycled 50 and 100 times, respectively (Fig. 6c and Supplementary Fig. 18), demonstrates that even after twice as many cycles the population of tetrahedral interstices in  $\text{Li}_2\text{RuO}_3$  does not reach the level of  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$ . Taking into account the lower rate of voltage decay for  $\text{Li}_2\text{RuO}_3$  compared with Ti-doped samples, this further supports the relationship between cation trapping at the tetrahedral interstices and voltage decay.

With respect to practical application, the migration of cations within the van der Waals gap (namely M in the  $\text{Li}_3$  layer) has





**Figure 6 | Comparison of HAADF-STEM images of  $\text{Li}_2\text{Ru}_{0.75}\text{M}_{0.25}\text{O}_3$  ( $\text{M} = \text{Sn}/\text{Ti}$ ) on long cycling. **a**,  $[\bar{1}\bar{1}0]$  HAADF-STEM image of the  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  sample after 50 charge-discharge cycles. Extra cations at the tetrahedral interstices next to the  $\text{LiM}_2$  layers appear locally (some marked with arrowheads). **b**,  $[\bar{1}\bar{1}0]$  HAADF-STEM image of the  $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$  sample after 100 charge-discharge cycles. On both images the intense cation disorder is visible within the  $\text{LiM}_2$  layers (appear brightest). Areas of the remaining order are also seen where pairs of bright dots alternate along the layers. **c**, HAADF-STEM signal profiles from areas outlined in the HAADF-STEM images. Green peaks associated with cation columns at the tetrahedral interstices are marked with arrowheads; yellow peaks of cation columns at the  $\text{Oc}_{\text{Li}}$  positions are marked with asterisks; blue peaks represent the octahedral  $\text{Oc}_{\text{LiM}_2}$  positions.**

1 been proved to be detrimental for cycling and rate capability  
 2 performances<sup>36,37</sup>. Here we believe that such migration is not  
 3 pernicious, because it is a cooperative migration probably initiated  
 4 by the formation of the peroxo-like groups that creates free  
 5 space thereby opening pathways for easy in- and out-of-plane  
 6 cation migration. Although the performances of such disordered  
 7 systems are surprising at first, it should be recalled that numerous  
 8 redox systems such as conversion or displacement reactions enlist  
 9 marked structural rearrangements, and even certain amorphous  
 10 compounds can also work efficiently<sup>38-41</sup>.

11 Together, our studies have shown  $\text{Li}_2\text{Ru}_{1-y}\text{Ti}_y\text{O}_3$  to be a model  
 12 system for exploring the complex interactions between cation

migration, structural rearrangements, creation of peroxo-like  
 species and voltage decay, and reveal attractive features as discussed  
 next in comparison with Sn-based or pure  $\text{Li}_2\text{RuO}_3$  phases.

We found for  $\text{Li}_2\text{Ru}_{1-y}\text{Ti}_y\text{O}_3$  phases an incomplete oxidation of  
 $\text{Ru}^{4+}-\text{Ru}^{5+}$  during the first 3.6 V plateau suggesting a competitive  
 anionic redox process that starts at a 200–300 mV lower voltage than  
 for the similar  $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$  electrode. Lowering of potential  
 has to be correlated with the significantly smaller volume of  
 $\text{Li}_{2-x}\text{Ru}_{1-y}\text{Ti}_y\text{O}_3$  compared with  $\text{Li}_{2-x}\text{Ru}_{1-y}\text{Sn}_y\text{O}_3$ , which increases  
 the  $\text{Ru}(4d)-\text{O}(2p)$  band overlap and therefore the covalent character  
 of Ru–O bonds. Moreover, Ti and Sn substitutions, in spite of  
 the fact that neither  $\text{Sn}^{4+}$  nor  $\text{Ti}^{4+}$  has free  $d$  electrons,



1 play different roles on the  $\text{Li}_{2-x}\text{Ru}_y\text{M}_{1-y}\text{O}_3$  ( $\text{M} = \text{Ti}/\text{Sn}$ ) band  
2 structures. Whereas the  $\text{Sn}(5s, 5p, 5d)$  bands are too high in  
3 energy to overlap with the  $\text{O}(2p)$  bands, the low-lying empty  $\text{Ti}(3d)$   
4 bands allow this overlap that raises the O–O anti-bonding band  
5 (Supplementary Fig. 19). These structural and electronic features  
6 not only enable the oxidation of oxo-ligands to peroxo-like species  
7 at lower potential for the Ti-substituted samples but also limit the  
8 flexibility of the oxygen lattice, which is therefore more prone to  
9  $\text{O}_2$  release than for the Sn-substituted samples, as confirmed by  
10 differential electrochemical mass spectroscopy experiments (data  
11 not shown).

12 Collectively, these data establish a robust correlation between  
13 the voltage decay shown by Li-rich  $\text{Li}_2\text{Ru}_{1-y}\text{M}_y\text{O}_3$  phases and the  
14 amount of cations that remain locked in tetrahedral sites. The  
15 largest decay was observed for  $\text{Ti}^{4+}$ , which owing to its smaller size  
16 compared with  $\text{Sn}^{4+}$ , is more prone to migrate via an intermediary  
17 tetrahedral site and hence to be trapped. Cation migration in layered  
18 oxides has been the subject of theoretical studies that have predicted  
19 several migration paths enlisting the migration of cations from  
20  $\text{O}_{\text{C}_{\text{LiM}_2}}$  to  $\text{O}_{\text{C}_{\text{Li}_3}}$  sites either directly or via intermediary tetrahedral  
21 sites with the latter one being energetically favourable<sup>25,42</sup>. Therefore,  
22 we decided to revisit such calculations which because it was not  
23 known at that time were done without considering the reversible  
24 formation of a peroxo-like group in these Li-rich compounds.

25 Density functional theory (DFT) calculations performed  
26 on the present  $\text{Li}_1\text{Ru}_{1/2}\text{M}_{1/2}\text{O}_3$  ( $\text{M} = \text{Ru}, \text{Ti}, \text{Sn}$ ) compounds  
27 (see Table in Supplementary Fig. 20) confirm that  $\text{Ti}^{4+}$  is  
28 the only cation stable in a tetrahedral coordination at this  
29 Li composition. More interestingly, the  $\text{LiRu}_{0.5}\text{Ti}_{0.5}\text{O}_3$  relaxed  
30 structure shows a spontaneous migration of  $\text{Ti}^{4+}$  cations from  
31  $\text{O}_{\text{C}_{\text{LiM}_2}}$  to  $\text{Td}_{\text{LiM}_2}$ , concomitantly with the formation of peroxo-  
32 like groups (Supplementary Fig. 20b) whereas the  $\text{Sn}^{4+}$  ions in  
33  $\text{LiRu}_{0.5}\text{Sn}_{0.5}\text{O}_3$  remain in their  $\text{O}_{\text{C}_{\text{LiM}_2}}$  sites in accordance with  
34 our experimental findings. In contrast, for pure  $\text{LiRuO}_3$  the  $\text{Ru}^{5+}$   
35 spontaneously migrates from  $\text{Td}_{\text{Li}_3}$  or  $\text{Td}_{\text{LiM}_2}$  to  $\text{O}_{\text{C}_{\text{Li}_3}}$ , the latter  
36 showing equivalent thermodynamic stability to  $\text{O}_{\text{C}_{\text{LiM}_2}}$  (to 23 meV).  
37 This suggests a low kinetic barrier for the  $\text{O}_{\text{C}_{\text{LiM}_2}} \rightarrow \text{O}_{\text{C}_{\text{Li}_3}} \rightarrow \text{O}_{\text{C}_{\text{LiM}_2}}$   
38 path in this system, perfectly consistent with the enlarged  
39 migration pathway resulting from the formation of peroxo-like  
40 species (Supplementary Fig. 20c). For the fully charged material  
41  $\text{RuO}_3$ , we note that the tetrahedral sites become more favourable  
42 than the  $\text{O}_{\text{C}_{\text{Li}_3}}$  and as favourable as the  $\text{O}_{\text{C}_{\text{LiM}_2}}$ , in perfect agreement  
43 with our microscopy results showing some Ru in tetrahedral sites  
44 after long cycling (see Table in Supplementary Figs 20 and 21).

45 In summary, we show that cation migration is an intrinsic  
46 and inseparable part of the charge–discharge process in the  
47 Li-rich phases and also that the continuous reduction in the  
48 averaged cell voltage is nested in the trapping of metal ions in  
49 tetrahedral sites that seem to favour the stability of delithiated  
50 structures. Although no straightforward solution yet exists, this  
51 study suggests research directions that may help obviate the  
52 voltage decay issue. One route is to increase the amount of  
53 large spectator ions, such as tin, to slow down or prevent the  
54 Td trapping. Tin's beneficial effect is demonstrated by a  
55 50% decrease in voltage fading when increasing the amount of  
56 Sn from 25% to 50% (Fig. 2b,c), but this is at the expense  
57 of an energy density penalty rendering this approach poorly  
58 attractive. An alternative is the use of electro-active cations  
59 larger than Ru while ensuring strong  $d$ – $sp$  hybridization to take  
60 advantage of the additional  $\text{O}^{2-} \rightarrow \text{O}_2^{2-}$  redox capacity. This can  
61 be realized by moving to  $4d$  metals such as Mo or Nb. Recent  
62 work on new cation-disordered rock-salt phases  $\text{Li}_{1.3}\text{Nb}_{1-x}\text{M}_x\text{O}_2$   
63 (ref. 43) having capacities approaching  $300 \text{ mAh g}^{-1}$  validates  
64 our reasoning although the long-term cycling of such phases  
65 is not yet reported. We hope this better understanding of the  
66 voltage decay phenomenon will provide clues to chemists for

identifying formulations to harvest all advantages of this new class  
of high-capacity electrodes based on dual cationic and anionic  
redox mechanisms.

## Methods

**Synthesis of  $\text{Li}_2\text{Ru}_{1-y}\text{Ti}_y\text{O}_3$  ( $0 \leq y \leq 1$ ).** Stoichiometric amounts of  $\text{RuO}_2$   
(Sigma-Aldrich 99.9%) and  $\text{TiO}_2$  (Sigma-Aldrich 98%) were homogenized, using  
a mortar and pestle for 20 min and then ball milled for 40 min with a 10 wt%  
excess of  $\text{Li}_2\text{CO}_3$  (Sigma-Aldrich, purity 99.0%) to compensate its volatilization at  
high temperature. The resultant mixture was heated at  $800^\circ\text{C}$  for 24 h with  
intermediate grinding. Furnace heating and cooling rate was maintained at  
 $2^\circ\text{C min}^{-1}$ .

**XRD.** XRD patterns were recorded using a Bruker D8 diffractometer equipped  
with a  $\text{Cu K}\alpha$  radiation source ( $\lambda_1 = 1.54056 \text{ \AA}$ ,  $\lambda_2 = 1.54439 \text{ \AA}$ ) and a LynxEye  
detector operated at 40 kV and 40 mA. The powder XRD patterns were refined  
using the Rietveld method<sup>44</sup> as implemented in the FullProf program<sup>45</sup>. *In situ*  
XRD analysis was carried out in a specially made Swagelok-type stainless-steel  
cell with an X-ray-transparent Be window. An aluminium foil was used between  
the Be window and the active material to prevent the oxidation of Be at higher  
operating voltages. High-resolution synchrotron powder diffraction patterns were  
collected on powders sealed under argon in glass capillaries of 0.8 mm diameter.  
The data were collected at the 11-BM beamline through the mail-in program at  
the Advanced Photon Source, ANL using a beam of wavelength  $0.41 \text{ \AA}$ .

**Electrochemical insertion/extraction of  $\text{Li}^+$ .** Electrochemical tests versus Li  
were done in Swagelok-type cells. The cells were assembled in an argon-filled  
glove box, using a ball-milled mixture of pristine material ( $\text{Li}_2\text{Ru}_{(1-y)}\text{M}_y\text{O}_3$ ,  
 $\text{M} = \text{Ti}/\text{Sn}/\text{Ru}$ ) with 10% of SP carbon as the positive electrode and a Li metal  
disc as the negative electrode. A Whatman GF/D borosilicate glass fibre sheet  
separator saturated with 1 M  $\text{LiPF}_6$  solution in a mixture of ethylene carbonate,  
propylene carbonate and dimethyl carbonate in a 1:1:3 ratio by weight (LP100)  
was employed. The mechanical mixing was performed under an argon  
atmosphere using a Spex-800 mixer-mill. Galvanostatic charge–discharge tests  
were conducted at  $20^\circ\text{C}$  using a Mac-Pile or a VMP system (Biologic S.A.)  
operating in galvanostatic mode. Unless otherwise specified, the cells were  
typically cycled between 4.6 and 2 V versus  $\text{Li}^+/\text{Li}^0$  at 1  $\text{Li}^+$  exchanged per 5 h  
(C/5). All of the results reported herein have been reproduced at least twice.

**XPS data collection and analysis.** XPS measurements were carried out using a  
Kratos Axis Ultra spectrometer connected through a transfer chamber to an  
argon-filled dry box. The samples were carefully transferred to the XPS  
spectrometer without any exposure to air/moisture and were analysed using  
monochromatized  $\text{Al K}\alpha$  radiation (1,486.6 eV). The pressure in the analysis  
chamber was maintained at around  $5 \times 10^{-9}$  mbar. Short acquisition time spectra  
were recorded before each experiment to analyse the stability of the sample under  
irradiation and then the normal spectra were collected with a constant pass  
energy of 20 eV. The binding energy scale was calibrated using the C 1s peak at  
285.0 eV and the peak positions and areas were optimized by a weighted  
least-squares fitting method using 70% Gaussian, 30% Lorentzian line shapes.  
Quantification was performed on the basis of Scofield's relative sensitivity factors.

**EPR spectra.** EPR spectra were recorded using a Brüker ELEXSYS E580  
spectrometer at 5 mW microwave power and 5G modulation amplitude. The  
measurements were carried out at room temperature and at 4 K.

**Transmission electron microscopy.** The samples were handled in an Ar-filled  
glove box. TEM specimens were prepared in the glove box by crushing the  
crystals in a mortar in anhydrous hexane and depositing drops of suspension  
onto holey carbon grids. The specimens were transported to the microscope  
column completely excluding contact with air. Electron diffraction patterns were  
obtained with a Tecnai G<sup>2</sup> electron microscope operated at 200 kV.  
HAADF-STEM images were obtained with aberration-corrected Titan G<sup>3</sup>  
electron microscopes operated at 200 kV using a convergence semi-angle of  
 $21.6 \text{ mrad}$ . The HAADF inner collection semi-angle was  $70 \text{ mrad}$ .

**DFT +  $U$  calculations.** Spin-polarized DFT +  $U$  ( $U_{\text{eff}} = 4 \text{ eV}$  for Ru) calculations  
were performed using the VASP code<sup>46,47</sup> and the GGA-PBE functional<sup>48</sup>. The  
plane-wave energy cutoff was set to 600 eV and the Brillouin zone integration was  
done in a  $k$ -point grid distributed as uniformly as possible. All atom coordinates  
and lattice parameters were fully relaxed using conjugate gradient energy  
minimization until the forces acting on each atom were less than  $5 \times 10^{-3} \text{ eV \AA}^{-2}$ .



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## Author contributions

M.Sathiyaraj, K.R., C.P.L. and A.S.P. carried out the synthesis, M.Sathiyaraj, and J.-M.T. conducted the electrochemical work and J.-M.T. designed the research approach; G.R. analysed the crystal structures and diffraction patterns; A.M.A. and G.V.T. carried out, analysed and exploited the electron diffraction and HAADF-STEM studies; D.F. and D.G. collected and analysed the XPS spectra; M.Saubanère and M.L.D. conducted the DFT calculations and developed the theoretical framework; M.Sathiyaraj, A.M.A. and J.-M.T. wrote the manuscript and all authors discussed the experiments and final manuscript.

## Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at [www.nature.com/reprints](http://www.nature.com/reprints). Correspondence and requests for materials should be addressed to J.-M.T.

## Competing financial interests

The authors declare no competing financial interests.