The influence of large cations on the electrochemical properties of tunnel-structured metal oxides

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Metal oxides with a tunnelled structure are attractive as charge storage materials for rechargeable batteries and supercapacitors, since the tunnels enable fast reversible insertion/extraction of charge carriers (for example, lithium ions). Common synthesis methods can introduce large cations such as potassium, barium and ammonium ions into the tunnels, but how these cations affect charge storage performance is not fully understood. Here, we report the role of tunnel cations in governing the electrochemical properties of electrode materials by focusing on potassium ions in α-MnO2. We show that the presence of cations inside 2 × 2 tunnels of manganese dioxide increases the electronic conductivity, and improves lithium ion diffusivity. In addition, transmission electron microscopy analysis indicates that the tunnels remain intact whether cations are present in the tunnels or not. Our systematic study shows that cation addition to α-MnO2 has a strong beneficial effect on the electrochemical performance of this material.
Metal oxides with an internal tunnel structure such as \( \alpha \)-MnO\(_2\), TiO\(_2\) and \( \beta \)-FeOOH are widely used for charge storage in rechargeable batteries and supercapacitors where charge carriers such as Li\(^+\), Na\(^+\) and Mg\(^2+\) can be reversibly inserted and extracted\(^2\)–\(^5\). Of these oxides, \( \alpha \)-MnO\(_2\), which possesses the typical octahedral molecular sieve structure, is characterized by well-ordered one-dimensional 1 \( \times \) 1 and 2 \( \times \) 2 tunnels\(^3\), as illustrated in Supplementary Fig. 1. The 2 \( \times \) 2 tunnel (4.6 \( \times \) 4.6 Å) is large enough to accommodate charge carriers such as Li\(^+\), Na\(^+\) and Mg\(^2+\), enabling fast ion diffusion inside the tunnel cavity\(^6\). In addition, Mn-based oxides are low cost, environmentally friendly and safer with respect to overcharge conditions compared with Co-based oxide electrodes\(^7\). Consequently, \( \alpha \)-MnO\(_2\) has been extensively studied as a promising cathode material for lithium (sodium and magnesium) ion batteries\(^8\)–\(^11\), lithium air batteries\(^12\),\(^13\) and supercapacitors\(^14\)–\(^16\).

Recent research shows that large cations such as K\(^+\), Ba\(^2+\) and NH\(_4\)^+ can be introduced during synthesis of \( \alpha \)-MnO\(_2\) (refs \(17\),\(^18\)). These cations, which partially occupy the tunnel cavities at certain stabilized lattice sites, are expected to interact with the charge carrier (Li\(^+\), Na\(^+\) and Mg\(^2+\)) and thus affect the charge storage performance of \( \alpha \)-MnO\(_2\) where tunnel-driven (de)intercalation contributes to the overall capacity\(^16\),\(^18\)–\(^20\). Despite considerable research devoted to improving the charge storage performance of \( \alpha \)-MnO\(_2\), the underlying mechanism by which tunnel cations affect the insertion/extraction of charge carriers is poorly understood.

In the case of Li\(^+\) being the charge carrier, many researchers believe that the presence of large cations (K\(^+\), Ba\(^2+\) and NH\(_4\)^+) can be introduced during synthesis of \( \alpha \)-MnO\(_2\) (refs \(17\),\(^18\)). These cations, which partially occupy the tunnel cavities at certain stabilized lattice sites, are expected to interact with the charge carrier (Li\(^+\), Na\(^+\) and Mg\(^2+\)) and thus affect the charge storage performance of \( \alpha \)-MnO\(_2\) where tunnel-driven (de)intercalation contributes to the overall capacity\(^16\),\(^18\)–\(^20\). Despite considerable research devoted to improving the charge storage performance of \( \alpha \)-MnO\(_2\), the underlying mechanism by which tunnel cations affect the insertion/extraction of charge carriers is poorly understood.

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In this report, nanowires of K\(^+\)-doped \( \alpha \)-MnO\(_2\) are hydrothermally synthesized and the K\(^+\) concentration is controlled and differentiated by acid solution treatment. The effect of varying K\(^+\) concentration on the rate performance of a Li/\( \alpha \)-MnO\(_2\) battery is studied systematically by measuring the electronic conductivity and Li\(^+\) diffusivity in the \( \alpha \)-MnO\(_2\) cathode. The underlying mechanism is revealed using a powerful combination of aberration-corrected scanning transmission electron microscopy (ACSTEM), transmission electron microscopy (TEM), electrical response measurements of single \( \alpha \)-MnO\(_2\) nanowires, electrochemical impedance spectroscopy (EIS) and density functional theory (DFT) simulations.

**Results**

**Structural characterization of \( \alpha \)-K\(_2\)MnO\(_2\).** Hydrothermally synthesized \( \alpha \)-MnO\(_2\) nanowires were characterized using ACSTEM, and the results are shown in Fig. 1. It can be seen from Fig. 1a,b that the \( \alpha \)-MnO\(_2\) nanowire is monocristalline, growing in the [001] direction with a uniform diameter. The [100] atomic resolution high-angle annular dark field (HAADF) image in Fig. 1c shows the 2 \( \times \) 2 tunnels (dark stripes) surrounded by two Mn atomic columns (yellow spheres) corresponding to the tunnel walls on each side. It can also be seen that the 2 \( \times \) 2 tunnels are decorated with ordered K atomic columns (pink spheres) around their centre positions, based on which the [001] atomic model is provided in Fig. 1d. K\(^+\) ions are successfully introduced during synthesis because excess K\(^+\) ions are present in solution to support the 2 \( \times \) 2 tunnels during their initial formation. The down-tunnel image of one \( \alpha \)-MnO\(_2\) nanowire (Fig. 1e) shows that the nanowire has a square shaped cross-section with four [100] lateral surfaces. The corresponding crystal structure is shown in Fig. 1f, in which 1 \( \times \) 1 and 2 \( \times \) 2 tunnels are clearly observed. 1 \( \times \) 1 tunnels are essentially empty while each 2 \( \times \) 2 tunnel is found to contain one atomic column, in good agreement with the lateral HAADF image in Fig. 1c. The energy-dispersive spectroscopy (EDS) along the [110] direction shown in Fig. 1f confirmed the tunnel walls to be Mn and the central atoms inside the 2 \( \times \) 2 tunnels to be K\(^+\) (Wyckoff 2a positions), from which the atomic model shown in the bottom inset of Fig. 1f was constructed. From these observations, the K\(^+\) concentration in as-synthesized \( \alpha \)-MnO\(_2\) was determined to be K\(_{0.25}\)MnO\(_2\).

The structural and compositional analyses of the nanowires after HNO\(_3\) treatment are carried out using X-ray powder diffraction (XRD) with Rietveld refinement and analytical STEM with EDS. The XRD results are shown in Fig. 2 with the refined lattice parameters and compositions shown in Supplementary Table 1. It can be seen that the \( \alpha \)-MnO\(_2\) phase is well maintained during the acid treatment as no extra peak generation or elimination is observed. However, with the increase of treatment time, all the peaks gradually shift toward higher angles, and this trend is more clearly demonstrated by the inset image showing the (200)\(_{\alpha}\)-MnO\(_2\) peak. The Rietveld refinement in the table quantifies the trend of tunnel contraction during acid treatment by deriving lattice parameters \( a \), \( b \) and \( c \), where the anisotropic tunnel expansion (mainly along \( a-b \) plane) is indicated. The estimated K\(^+\) concentration further confirms that the tunnel contraction is essentially determined by the gradual removal of K\(^+\) from the tunnels.

The atomic imaging of the tunnels with different K\(^+\) concentrations in Fig. 3 reveals that HNO\(_3\) treatment was effective in removing K\(^+\) from the 2 \( \times \) 2 tunnels, and the K\(^+\) concentration can be controlled by altering the treatment time. After 1-day treatment, K\(^+\) has been partially removed from the nanowire, and the 2 \( \times \) 2 tunnels are thus only partially filled. After 4-day treatment, \( \alpha \)-MnO\(_2\) is essentially free of any K\(^+\) ions, as confirmed by both the HAADF image showing no K\(^+\) contrast (Fig. 3c) and the lack of any K\(^+\) signal in the EDS spectra shown in the inset. The compositions of \( \alpha \)-MnO\(_2\) nanowires without treatment and after 1- and 4-day acid treatment were thus deduced to be K\(_{0.25}\)MnO\(_2\), K\(_{0.25}\)–MnO\(_2\) and undoped MnO\(_2\), respectively. It is also notable that the 2 \( \times \) 2 tunnels slightly contract after K\(^+\) removal, as indicated by the [020] spacing changing from 4.97 Å for the untreated nanowire to 4.84 Å for the 4-day treated nanowire. This tunnel contraction trend is clearly illustrated in Fig. 3d–f. Although the tunnel experiences significant volume change, the overall tunnelled structure of \( \alpha \)-MnO\(_2\) is still maintained after K\(^+\) removal, enabling all these three types of nanowires to function as an intercalation cathode in a lithium ion battery.

There is a slight variation between XRD and atomic STEM imaging in determining the K\(^+\) concentration and lattice constants. This is understandable considering that STEM focuses on local atomic structure of a single nanowire, while XRD provides average bulk information including the surface lattice and structural defects. In our case, since the composition of the nanowires without HNO\(_3\) treatment is determined by counting
the Mn and K atoms in the STEM image, which is mathematically more accurate than XRD, we have identified these nanowires as K$_{0.25}$MnO$_2$. This indicates that all 2a sites inside the $2 \times 2$ tunnels are occupied by K$^+$. For 1-day treated nanowires, we express the composition using K$_{(0.25 - x)}$MnO$_2$.

Previous studies suggest that the removal of K$^+$ from $2 \times 2$ tunnels in acid solutions is explained by either the K$^+$–H$^+$ exchange mechanism$^{27,28}$, Mn oxidation mechanism$^{23,29}$ or the existence of both$^{30}$. The critical difference between them is whether the Mn valence is increased or not. In our study, the dominant mechanism is found to be Mn oxidation to Mn$^{4+}$ rather than K$^+$–H$^+$ exchange. The detailed analyses of Mn valence change using electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS) are provided in Supplementary Figs 2 and 3, respectively, and the discussions are given in Supplementary Note 1. Both EELS and XPS confirm the existence of Mn$^{3+}$ in the nanowires before acid treatment (K$_{0.25}$MnO$_2$), while a portion of Mn$^{3+}$ gradually decreases with increase of treatment time. The average Mn valence gradually increases to Mn$^{4+}$ as a result of K$^+$ removal. The structural techniques of Raman, Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR) and inductively coupled plasma optical emission spectroscopy (ICP-OES) (Supplementary Fig. 4 and related discussions in Supplementary Note 2) are also provided to explore the chemical composition evolution during acid treatment, where the possibility of H$^+$ presence in the tunnels is found to be negligible, which again supports the postulate that K$^+$–H$^+$ exchange is not the dominant mechanism.

Figure 1 | Basic (S)TEM characterization of as-prepared $\alpha$-MnO$_2$ nanowires. (a,b) A low-magnification TEM image of the as-synthesized $\alpha$-MnO$_2$ nanowire and the corresponding [100] electron diffraction pattern; (c,d) The [100] HAADF image of the same nanowire with the representative atomic model. The yellow spheres indicate Mn atomic columns, while red and pink represent O and K$^+$ ions, respectively. (e) A low-magnification [001] TEM image showing one cross-section of $\alpha$-MnO$_2$ nanowire; (f) A [001] HAADF image revealing the atomic structure of tunnelled $\alpha$-MnO$_2$ with the red dotted square demarcating a $2 \times 2$ tunnel and the blue dotted square a $1 \times 1$ tunnel. The green line indicates the region along which EDS linear scanning was carried out. The bottom inset shows a model of the tunnel structure viewed down the tunnel axis. Scale bars: 50 nm in a, 1 nm in c,f, and 10 nm in e.

Figure 2 | XRD patterns of the three groups of nanowires after acid treatment over different timescales. The inset image is the enlarged view of the $\alpha$-MnO$_2$ (200) peak, where the gradual peak shift toward higher angle direction with increase of treatment time is observed.
Before the electrochemistry analysis, the surfaces and thermal stability of the nanowires were characterized to check whether the nanowires are affected by the acid treatment. The Brunauer–Emmett–Teller (BET) analysis given in Supplementary Table 2 (detailed discussions in Supplementary Note 5) and SEM images in Supplementary Fig. 5 show no significant change in the surfaces of nanowires. Thermogravimetric analysis (TGA) and in situ TEM heating techniques are used to test the thermal stability of the nanowires after K+ removal from the tunnels, and the results and detailed analysis are shown in Supplementary Figs 6 and 7, respectively, while the discussions are given in Supplementary Note 3. The results confirm that the nanowires after K+ removal from the tunnels are thermally stable without any phase transition or tunnel collapse up to 350 °C.

Effect of K+ on electronic and ionic conductivities. Our previous simulation work17 suggest that 2 × 2 tunnels are the preferred Li+ transport channels in pure α-MnO2. We have also reported previously that Li+ ions thermodynamically occupy the off-centred Wyckoff 8 h site inside each 2 × 2 tunnel rather than the tunnel centre4,17, which is also demonstrated by other groups33,34. Therefore, with K+ on the centred 2a sites and the tunnel expanded by K+, it is reasonable to expect the K+ concentration inside the 2 × 2 tunnels to affect both electronic and ionic transport and hence the electrochemical behaviour of an α-MnO2 cathode. To examine these effects, the electronic conductivity and Li+ diffusivity of α-MnO2 nanowires with different K+ concentrations were characterized using in situ TEM and EIS methods.

The electronic structure was also examined by DFT simulations and also by direct electrical probing within the microscope, the results of which are given in Fig. 4a,b. This computational work complements and extends previous DFT studies8,16 on interstitial cation incorporation in α-MnO2. The simulated density of states (shown in Fig. 4a) indicates that pure α-MnO2 has a bandgap of ~2.8 eV suggesting semiconductor behaviour, and agrees well with the reported value of Young et al.16 For K0.25MnO2, newly formed occupied states appear inside the original MnO2 bandgap, indicating mixed Mn4+/Mn3+ in K0.25MnO2, which is compatible with previous reports32. This indicates that the presence of K+ inside the 2 × 2 tunnels can enhance the electronic conductivity of α-MnO2 through electron hopping between Mn4+/Mn3+.

For each K+ concentration, the conductivity of three nanowires was measured to test reproducibility. The I–V responses of all the nanowires with different K+ concentrations measured in situ in the microscope (inset of Fig. 4b) are nonlinear but symmetric in the low-bias regime. This can be ascribed to the Schottky barriers formed between the semiconducting nanowire and the metal (W) electrodes33. In the large-bias regime (8–10 V), the I–V curves exhibit a near-linear relationship, and the conductance (G) of the nanowires can be calculated according to $G = dI/dV$ (ref. 34). G was calculated to be 0.15–0.19 μS for K0.25MnO2, 0.025–0.034 μS for K0.25−xMnO2 and 0.0011–0.0050 μS for undoped MnO2; the results are plotted in Fig. 4b, and details of the data fitting are provided in Supplementary Table 3. Because of the similar diameters and lengths of the selected nanowires used for testing, the conductivities of nanowires with different K+ concentrations should exhibit similar trends as the conductance. It can be seen that K0.25MnO2 has a conductivity about 40 times higher than that of pure α-MnO2, indicating the important role of tunnel cations in enhancing the electronic conductivity of α-MnO2 nanowires. The origin of the improved electronic conductivity of α-MnO2 containing K+ can be attributed to the electron hopping between heterovalent Mn pairs (Mn4+/Mn3+) induced by K+ doping35,36. Increasing the cation content will produce more regions inside the nanowire with mixed Mn3+/Mn4+ valence states, resulting in higher electronic conductivity37.

Li+ diffusion in α-MnO2 nanowires with different K+ contents was characterized by EIS, and the results are shown in...
were tested for each \( K \) of the nine electrodes with \( K_{0.25} \). The simulation results using the equivalent circuit shown in Fig. 4c,d. Figure 4c shows the impedance spectra (Nyquist plots) and (d) linear fitting to \( Z' = \omega^{-1/2} \) plots in the low frequency range (<25 Hz) of the electrodes with \( K_{0.25} \), \( K_{0.25-} \) or undoped \( MnO_2 \) as the active material. The scatter points are the experimental data and the lines represent the simulation results using the equivalent circuit shown in c.

**Table 1 | Transport properties derived from the impedance spectra (at \( T = 25^\circ C \).**

| Samples          | \( R_\text{e} (\Omega) \) | \( R_\text{ct} (\Omega) \) | \( \sigma (\Omega\text{s}^{-1/2}) \) | \( D_\text{Li} (\text{cm}^2\text{s}^{-1}) \) |
|------------------|---------------------------|---------------------------|-------------------------------|----------------------------------|
| \( K_{0.25} \)  | 9.916                     | 97.26                     | 47.10                         | \( 1.91 \times 10^{-12} \)       |
| \( K_{0.25-} \) | 8.198                     | 246.3                     | 133.5                         | \( 7.16 \times 10^{-13} \)       |
| Pure \( MnO_2 \) | 7.261                     | 182.2                     | 160.5                         | \( 2.82 \times 10^{-15} \)       |

Fig. 4c,d. Figure 4c shows the impedance spectra (Nyquist plots) of electrodes with \( K_{0.25} \), \( K_{0.25-} \) or undoped \( MnO_2 \) as the active material. The low frequency region the real part of the impedance \( (Z') \) is linear against the \(-1/2\) power of the angular frequency \( (\omega^{-1/2}) \), and the slope is called the Warburg coefficient \( (\sigma) \). Linear fits to the \( Z' = \omega^{-1/2} \) plots for the untreated and treated \( \alpha-MnO_2 \) electrodes are shown in Fig. 4d, and the corresponding \( \sigma \) values are listed in Table 1. In addition, the equivalent circuit (inset of Fig. 4c) was used to fit the spectra and the results are listed in Table 1. The charge-transfer resistance \( (R_{\text{ct}}) \) increased after \( K^+ \) removal, indicating that doping with \( K^+ \) enhances lithium intercalation near the electrode/electrolyte interface.

The chemical diffusion coefficient of \( Li \) ions \( (D_{\text{Li}}) \) inside an electrode can be derived using the following equation

\[
D_{\text{Li}} = \frac{1}{2} \left( \frac{V_m \text{dE}}{F \sigma \text{dy}} \right)^2, \tag{1}
\]

where \( V_m \) is the molar volume of the active material, \( F \) is the Faraday constant, \( S \) denotes the active surface area of the positive electrode and \( d\text{E}/dy \) is the slope of the open circuit potential versus the \( Li^+ \) concentration \( y \) in \( Li,K,MnO_2 \). The value of \( d\text{E}/dy \) was obtained from galvanostatic intermittent titration technique (GITT) measurements. The specific surface areas were obtained from BET results (Supplementary Table 2), with 28.2 m²g⁻¹ for \( K_{0.25} \), 26.8 m²g⁻¹ for \( K_{0.25-} \) and 26.7 m²g⁻¹ for Pure \( MnO_2 \) after 1-day acid treatment and 26.7 m²g⁻¹ for Pure \( MnO_2 \) after 4-day treatment, respectively. The measured values agree well with reported specific surface areas for hydrothermally synthesized \( \alpha-MnO_2 \) nanostructures which is in the range of 20–40 m²g⁻¹ (refs 12,39–41). The values of \( D_{\text{Li}} \) are listed in Table 1 showing that the chemical diffusion coefficient of \( Li^+ \) is reduced by
removal of K⁺. In addition, extending the time of acid treatment from 1 day to 4 days leads to a three-orders-of-magnitude decrease in the value of $D_{MnO2}$. These results directly confirm that K⁺ in $\alpha$-MnO₂ tunnels facilitates diffusion of Li⁺. Although there are currently no measured diffusion data on Li/K-MnO₂ for direct comparison, the magnitudes of $D_{MnO2}$ are comparable to other electrode materials; for example, experimental diffusion coefficients of $10^{-8}$ to $10^{-12}$ cm² s⁻¹ have been reported for Li⁺ diffusion in layered oxide cathodes such as LiCoO₂ and Li(Ni,Mn,Co)O₂ (refs 42–44). The increase of Li⁺ diffusivity by the addition of K⁺ can be attributed mainly to the expansion of the tunnel cavity by the large centred K⁺ cation at 2a sites. The improved e⁻ conductivity is also beneficial for Li⁺ conductivity in the tunnels with the presence of K⁺.

### Rate performance of $\alpha$-KₓMnO₂ cathodes

Since the presence of tunnel cations improves both the electronic conductivity and Li⁺ diffusivity of $\alpha$-MnO₂, the rate performance of a Li/$\alpha$-MnO₂ battery would be expected to be enhanced when K⁺ occupy the tunnels. Before we examined the rate performance, the tunnel stability as well as the stability of K⁺ inside the tunnels during repetitive cycling are characterized. Supplementary Fig. 8a–c shows the morphology and phase analysis of three groups of nanowires (K₀.₂₅MnO₂, K₀.₂₅–xMnO₂, pure MnO₂) after 100 battery cycles (Li/$\alpha$-KₓMnO₂ coin cells). Supplementary Fig. 8d shows the EDS quantification of K⁺ concentrations inside the tunnels before and after battery cycles for the electrode initially composed of K₀.₂₅MnO₂ nanowires. The K⁺ concentration in the tunnels is slightly reduced after cycling (probably lost into the electrolyte), while the majority of K⁺ remains inside the nanowires. All the nanowires, including those with K⁺ (partially and totally) removed, retain their tunnelled $\alpha$-MnO₂ structure with no obvious morphology change during battery cycling. Therefore the good stability of K⁺ ions in the tunnels can retain their effect on the battery performance upon continuous cycling.

To investigate the effect of K⁺ concentration on the first cycle performance, the galvanostatic discharge/charge curves for three groups of nanowires are shown in Supplementary Fig. 9. While all exhibit a discharge reaction around 2.5 V versus Li/Li⁺, the discharge capacity of the nanowires without acid treatment (143 mAh g⁻¹) is relatively lower than that of the treated nanowires (157 and 170 mAh g⁻¹), which can be ascribed to the addition of inactive mass of K⁺ into the electrode. Upon charge, however, the capacity of the treated nanowires is lower than the capacity of the nanowires with no treatment. To study the rate performance, the first discharge capacity of a Li/$\alpha$-MnO₂ battery under different current rates (0.1, 0.5, 1, 2 and 5 C) was measured for the three groups of nanowires. To make the comparison more straightforward, the discharge capacity at 0.1 C was normalized to 100%. From Fig. 5a, it can be seen that the first discharge capacities of cathodes made of K₀.₂₅MnO₂, K₀.₂₅–xMnO₂ and undoped MnO₂ were all reduced when the C rate was increased from 0.1 to 5 C. The capacity retention behaviour under high discharge currents, however, varied with different K⁺ concentrations. Li/K₀.₂₅MnO₂ exhibited 62% capacity retention at 5 C, while Li/K₀.₂₅–MnO₂ retained only 54% capacity and Li/MnO₂ showed capacity retention as low as 8% at 5 C. The cycling-rate performance of the three groups of nanowires is shown in Supplementary Fig. 10 with the detailed discussions given in Supplementary Note 4. While the capacity retention is similar for the three groups at lower current, it shows gradually better capacity retention at higher currents (2 C and 5 C) for the nanowires with the higher K⁺ concentration. As discussed earlier, the presence of K⁺ in tunnelled $\alpha$-MnO₂ not only improves electronic conductivity by boosting e⁻ hopping via Mn³⁺/Mn⁴⁺ couples, but also enhances Li⁺ diffusivity. The detailed mechanism is illustrated in Fig. 5b.

Our investigation opens up further research opportunities in this area. For example, although not a trivial task, future atomistic simulations could be used to explore Li-ion diffusion in these nanowire structures with large cations inside. It would also be interesting to explore replacing K⁺ with other cations such as Ag⁺, Ba²⁺, to examine models related to cation-tunnel interactions, such as charge-switching states proposed by Young et al.¹⁶, and to study the effect of trace amounts of H⁺ via sensitive techniques such as quasi-elastic neutron scattering. Currently, we have found no experimental evidence showing the direct capacity contribution from Li⁺ intercalation into 1 x 1 tunnels, although future work could explore this possibility as a
competing mechanism to insertion into 2 × 2 tunnels where large cations reside.

Discussion
In this study, the effect of tunnel cations (K⁺) on the electrochemical performance of α-MnO₂ cathodes was examined using a powerful combination of analytical ACSTEM, in situ TEM, electrochemical testing and ab initio modelling. α-MnO₂ nanowires with different K⁺ concentrations were prepared and imaged at sub-Ångstrom resolution to determine the structure of tunnels as well as the location and content of K⁺. It was found that the presence of K⁺ inside the 2 × 2 tunnels of α-MnO₂ nanowires improves both their electronic conductivity and Li⁺ diffusivity. These enhancements facilitate favourable electrode kinetics, and thus result in good rate performance of Li/α-MnO₂ based batteries.

The results of our systematic study provide a valuable framework for the rational selection of tunnel cations and their concentrations to improve the rate performance of tunnel-based intercalation electrodes. In addition, the favourable effect of K⁺ incorporation suggests that further exploration of tunnel-based cathodes with new battery chemistries based on Na⁺, Mg²⁺, and Al³⁺ ions is also warranted.

Methods

Materials synthesis and composition control. α-MnO₂ nanowires were synthesized hydrothermally using KMnO₄ and MnSO₄ as reactants in aqueous solution. Specifically, 0.9878 g of KMnO₄ and 0.4226 g of MnSO₄·H₂O were dispersed in 80 ml of deionized (DI) water under constant stir for 30 min to form a purple solution. The obtained slurry was then transferred to a 100 ml Teflon-lined stainless steel autoclave, sealed and heated at 160 °C for 12 h. The synthesized nanowires were first separated from the solution by centrifugation, then washed with DI water and ethyl alcohol, and finally dried in air at 60 °C.

In situ TEM testing of the α-MnO₂ nanowires was done inside a JEOL 3010 TEM. The nanowires were first dispersed onto a TEM grid and then mounted to an in situ heating holder. After loaded into TEM chamber, the nanowires were heated to 450 °C with the rate of 10 °C/min⁻¹. Data were collected at 25, 200, 280, 350, 400 and 450 °C after maintaining samples at each specific temperature for 5 min.

Electrochemical testing. The electrode slurry was made of 80 wt% α-MnO₂ nanowires, 10 wt% super P carbon and 10 wt% polyvinylidene difluoride binder in N-methyl- pyrrolidinone (NMP). The mixture was then cast onto an Al foil to make the electrode. The electrode was dried at 75 °C for 4 h, followed by thorough drying at 75 °C overnight under vacuum. Electrochemical measurement of the first discharge capacity was carried out using CR2032 coin cells with Li metal as the counter electrode, 1.2 M LiPF₆ in EC/EMC (3/7 by weight) as the electrolyte, and Celgard 2325 membrane as the separator. Cells were cycled between 1.5 and 4 V at different rates.

Electrochemical impedance data were collected with a Solartron 1470E and 1451A cell testing system, using a 5 mV AC perturbation with frequencies ranging from 100 kHz to 0.1 Hz. A three-electrode system was used so that the spectra obtained correspond to the impedance of the cathode side only. A Li metal wire was used as the reference electrode and a piece of Li foil was used as the counter electrode. Spectra were fit according to the equivalent circuit in Fig. 4a, where Rᵣ is the electrolyte resistance, Rₑ is the charge-transfer resistance, Cₓ is the double layer capacitance that takes the roughness of the particle surface into account and Zₓ is the Warburg diffusive impedance. The semicircle in the high frequency region of the spectra represents the Warburg diffusion of Li⁺ into the bulk of cathode particles. GITT measurements were carried out with a negative current pulse at C/20 for 30 s, followed by relaxations for 5 h. This sequence of discharge pulse followed by a relaxation time was repeated until the potential reached 1.5 V. GITT curve is provided in Supplementary Fig. 11.

Data availability. The authors declare that the data supporting the findings of this study are available within the paper.
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Author contributions

Y.Y., J.L. and R.S.-Y. conceived the idea, and Y.Y. carried out the (S)TEM and in situ TEM experiments. K.C. and X.G. performed the electrochemical tests. H.A. contributed to the in situ EELS experiments. H.C. performed the XPS measurements. C.Z., K.A. and Y.Y. contributed to the interpretation of the results. Y.Y. and R.S.-Y. wrote the paper. All authors discussed the results and commented on the manuscript. All authors contributed equally to this work.
data were captured by K.H. and analysed by J.L. S.S.-A. did the TGA analysis. XRD data were analysed by C.Z., Z.Y. did the BET analysis. W.Y. synthesized the nanowires. X.L. did the Raman and IR analysis. H.W. did the NMR analysis. A.N. and B.S. provided necessary TEM support. H.C., S.M.W. and M.S.I. carried out the DFT calculations. Y.Y. and C.Z. wrote the paper under the direction of J.L., M.S.I. and R.S.-Y. All authors contributed to the analysis and writing of the final version of the paper.

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