A high-capacity cathode is the key to the realization of high-energy-density lithium-ion batteries. The anionic oxygen redox induced by activation of the Li$_2$MnO$_3$ domain has previously afforded an O3-type layered Li-rich material used as the cathode for lithium-ion batteries with a notably high capacity of 250–300 mAh g$^{-1}$. However, its practical application in lithium-ion batteries has been limited due to electrodes made from this material suffering severe voltage fading and capacity decay during cycling. Here, it is shown that an O2-type Li-rich material with a single-layer Li$_2$MnO$_3$ superstructure can deliver an extraordinary reversible capacity of 400 mAh g$^{-1}$ (energy density: $\approx$1360 Wh kg$^{-1}$). The activation of a single-layer Li$_2$MnO$_3$ enables stable anionic oxygen redox reactions and leads to a highly reversible charge–discharge cycle. Understanding the high performance will further the development of high-capacity cathode materials that utilize anionic oxygen redox processes.

The energy density of lithium-ion batteries is a key factor determining their use in portable electronic devices, electric vehicles, and large-scale energy storage. High-capacity cathode materials are extremely important for constructing high-energy-density lithium-ion batteries.$^{[1-3]}$ However, the low capacities of conventional Li-ion battery cathode materials, such as layered LiCoO$_2$ (140 mAh g$^{-1}$) and olivine LiFePO$_4$ (170 mAh g$^{-1}$), do not satisfy the performance requirements for the applications mentioned above. The emergence of O3-type Mn-based, distinguished by oxygen stacking of ABCABC mode, Li-rich layered oxides in recent years has given rise to great interest in Li-rich materials, which can deliver high capacities of up to 250–300 mAh g$^{-1}$. Some studies have provided evidence that this notably high capacity results from multiple electron transfers involving both cationic and anionic redox processes.$^{[4-6]}$ However, the anionic oxygen redox reactions induced by the activation of Li$_2$MnO$_3$ domains promotes transition metal ion migration, leading to the transition of the layer to spinel phases and demonstrating severe voltage and capacity decays during cycling, which are the major obstacles preventing industrial applications.$^{[7,8]}$ Therefore, the synthesis of new cathode materials that can enhance the energy density of Li-ion batteries is still one of most challenging issues that must be resolved.

In this study, we prepared a new O2-type, by oxygen stacking of ABBA mode, Mn-based, Li-rich oxide with a single-layer Li$_2$MnO$_3$ superstructure, which demonstrated a reversible capacity of $\approx$400 mAh g$^{-1}$ with a stable discharge voltage and a high charge–discharge efficiency during cycling. It was obtained by means of ion exchange from Na$_{5/6}$Li$_{1/4}$M$_{3/4}$O$_x$ (M = Mn$_{0.75}$Co$_{0.25}$) in a molten salt mixture of LiNO$_3$/LiCl (88:12 w/w) at 280 °C for 4 h, as described in the Supporting Information. The formula of the as-prepared material was determined to be Li$_{1.25}$Co$_{0.25}$Mn$_{0.50}$O$_2$.

Figure 1a shows the X-ray diffraction (XRD) pattern for the well-crystallized Li$_{1.25}$Co$_{0.25}$Mn$_{0.50}$O$_2$ particles. The Rietveld refinement (Figure 1a) shows that three phases can be indexed from the diffraction patterns: O2-type Li$_2$MnO$_3$, O2-type LiCoO$_2$, and O4-type LiCoO$_2$, with corresponding phase content of 68.18, 17.16, and 14.46%, respectively. The high-angle annular dark-field (HAADF) image in the [001] crystal direction (Figure S2a,b, Supporting Information) also exhibits a honeycomb structure, which is the characteristic atomic distribution of a typical Li$_2$MnO$_3$ structure,$^{[5]}$ but in the stack of O2 type along the c-direction. The selected area electron diffraction (SAED) pattern (Figure 1b) captured along the [001] direction also shows an O2-Li$_2$MnO$_3$ feature. The Rietveld refinement results (Figure S3 and Tables S1–S3, Supporting Information) with $R_{wp}$ factors of 6.79% indicate that the main heavy atoms of the structure are correctly positioned. Therefore, it can be determined that the main phase of the as-prepared sample is O2-type stack (about 85.34%), with 14.46% O4 stack.

The HAADF scanning transmission electron microscopy image in Figure 2a further confirms the composite nanostructure of the as-prepared material. Because the image intensity is related to the atomic number and the number of atoms, the bright dots in Figure 2a represent the heavy atoms Co and Mn in Li$_{1.25}$Mn$_{0.50}$Co$_{0.25}$O$_2$, while light atoms Li and O...
are nearly invisible. Therefore, the discontinuous dots contrast (area I) indicates Li$_2$MnO$_3$-like areas and the continuous dots contrast (area II) denotes LiMo$_2$-like areas. Unlike the big distinguishing domain features of the Li$_{1/3}$Mn$_{2/3}$ slab in the O3-type LiMnO$_2$ slab reported previously,[9,10] most of the Li$_{1/3}$Mn$_{2/3}$ slab in the O2-type Li$_{1.25}$Co$_{0.25}$Mn$_{0.50}$O$_2$ is single-layer LiM$_6$ ordered along the [100] zone axis rather than in a domain. This means that the Li$_2$MnO$_3$ superstructure in the O2-type Li$_{1.25}$Co$_{0.25}$Mn$_{0.50}$O$_2$ is more uniformly dispersed in the matrix than that in the O3-type LiMnO$_2$. The activation of the Li$_2$MnO$_3$ domain will result in the formation of oxygen–oxygen dimers,[11–13] as a result of the unstable electrochemical behavior, whereas the single-layer Li$_2$MnO$_3$ superstructure can prevent the formation of oxygen–oxygen dimers. Density functional theory calculations show that once all the lithium ions are extracted from Li$_{1.25}$Co$_{0.25}$Mn$_{0.50}$O$_2$ with big Li$_2$MnO$_3$ domain, oxygen ion (O$^{2-}$) dimerization occurs (O–O bond length 1.38 Å), and molecular dioxygen (O–O bond length 1.29 Å) is released in the O3-type Co$_{25}$Mn$_{0.50}$O$_2$, while the O–O bond length in the O2-type material Li$_{1.25}$Co$_{25}$Mn$_{0.50}$O$_2$ with single-layer Li$_2$MnO$_3$ is 2.44 Å, indicating a stable local oxygen structure during cycling (Figures S4 and S5, Supporting Information). Moreover, HAADF scanning (Figure 2b) reveals that the structure consists of stacks of O2 (blue vertical line) and O4 phases (red vertical line) along the c-axis, which may result from a stacking fault.[14,15] All these results suggest that the as-obtained Li$_{1.25}$Co$_{0.25}$Mn$_{0.50}$O$_2$ material is mainly an integrated O2-type LiMnO$_2$ composite with a single-layer O2-Li$_2$MnO$_3$ superstructure.

The transformation from the layer to the spinel phase is unfavorable because the oxygen lattice rearrangement requires all the Mn–O bonds in the O2-type structure to break.[16] Therefore, we expected that the O2-type structure stacking with the single-layer Li$_2$MnO$_3$ superstructure would be stable and demonstrate good reversibility with high capacity during cycling. Figure 3a shows that the as-prepared material can deliver a reversible capacity of up to 400 mAh g$^{-1}$ (energy density: $\approx$1360 Wh kg$^{-1}$) (energy density: $\approx$1360 Wh kg$^{-1}$). This is the highest reversible energy density reported for any known lithium-ion battery cathode material. Most importantly, although the oxygen anions participate in the redox reaction, the decrease in voltage after 50 cycles is only 0.07 V (Figure 3b). This is because the Mn ions cannot be transferred from an octahedral site to a tetrahedral site in the as-obtained Li$_{1.25}$Co$_{0.25}$Mn$_{0.50}$O$_2$ material, and there is no

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**Figure 1.** Characterization of the as-prepared Li$_{1.25}$Co$_{0.25}$Mn$_{0.50}$O$_2$ material. a) Rietveld refinement of room-temperature XRD using Topas 4.2 software. b) SAED patterns along [001] showing monoclinic character of Li$_{1.25}$Co$_{0.25}$Mn$_{0.50}$O$_2$.

**Figure 2.** a) HAADF image of the Li$_{1.25}$Co$_{0.25}$Mn$_{0.50}$O$_2$ particles. b) Magnified HAADF image of Li$_{1.25}$Co$_{0.25}$Mn$_{0.50}$O$_2$ along the [100] zone axis based on the P6$_{3}$mc space group.
layer-to-spinel transformation in O2-type materials over a prolonged cycle.

Note that the initial charge–discharge efficiency is as high as 99.5% for the as-prepared O2-type Li-rich materials, which favors sufficiently high battery energy density for practical applications (Figure 3a). In previous studies, O3-type, Li-rich materials have exhibited low initial charge–discharge efficiency due to the irreversible de-intercalation of the lithium that results from the evolution of oxygen in the Li2MnO3 activation process. Therefore, this high initial efficiency demonstrates that the local oxygen structure remains stable even though the oxygen anions play a major role in charge compensation in the unique single-layer Li2MnO3 superstructure.

Figure S7 (Supporting Information) shows the dQ/dV plots of the 2nd and 50th cycles for the O2-type Li-rich material electrode at a rate of 80 mA g\(^{-1}\) for the synthesized material. These curves are characterized by several broad peaks that reflect the redox behavior of the as-prepared material. The cathodic peaks at \(\approx 2.75\) and \(3.2\) V can be attributed to the Mn\(^{4+}/\text{Mn}^{3+}\) and Co\(^{4+}/\text{Co}^{3+}\) redox couples, respectively, and these couples have potentials lower than those in the O3-type Li-rich material (Figure S8, Supporting Information). The peak at \(\approx 4.0\) V corresponds to the O\(^{2-}/\text{O}^{-}\) anodic redox couple. Compared to the second cycle, the difference in the cathodic peak potentials of O2-type Li-rich after 50 cycles is less than 100 mV, which is less than that in the O3-type Li-rich electrode material. This finding shows that a Li-rich material with an O2 structure can stabilize the discharge voltage upon cycling. Note that the suppression of the voltage decay is an intrinsic property of an O2-type structure; that is, the O2 structure cannot transform into a spinel structure.

The Mn K-edge absorption spectra (Figure 3c) remain nearly constant for the first charge, implying that the Mn oxidation state remains at Mn\(^{4+}\), which is in agreement with the results obtained for the Mn L-edge (Figure S9c, Supporting Information) and similar to those for conventional layer-structured materials. The K-edge spectra of Co exhibit a continuous edge shift toward higher energy levels until a charging voltage of 4.4 V is applied, indicating an increase in the Co oxidation state from Co\(^{3+}\) to Co\(^{4+}\). After charging to the 4.5 V voltage plateau, a reverse shift is observed for the Co K-edge (Figure S10a, Supporting Information), indicating a possible modification of the Co local structure that induces strong electronic redistributions along the Co–O bonds. This is similar to the reductive coupling mechanism of Ru in Li2RuO3, which can enhance the stability of Li-rich cathode materials. (More details of charge compensation mechanism in the first cycle can be seen in the Supporting Information.)

The evolution of the pre-edge peak in the O K-edge spectra (Figure 3d) further confirmed that the as-obtained material is capable of stabilizing the oxygen holes generated by the Li removal while achieving a reversible O\(^{2-}/\text{O}^{-}\) redox. There is little change in the pre-edge peak of O (3.0–4.4 V), but the pre-edge peak increases significantly from 4.4 to 4.8 V, which is consistent with a previous report on oxygen anion redox reactions. Upon discharging (Figure S11, Supporting Information),
the pre-edge peak returned to its original position, and the peak area decreased, indicating that the redox process during the plateau stage can be mainly attributed to the O ions and is reversible during the charge–discharge process.

The Debye–Waller factor, σ (Mn−O), in Figure S12 (Supporting Information) exhibits a slight change before the voltage plateau (at ≈4.4 V), indicating that there is a small local structure change induced by lithium extraction from the LiMnO2 slabs. Upon further charging in the voltage plateau region, the σ (Mn−O) values also increase slightly during the initial charging process. This was different from the large increase in the σ (Mn−O) values previously reported for O3-type Li-rich layered oxides at this stage. This is because the Li2MnO3 in the as-prepared O2-type Li$_{1.25}$Co$_{0.25}$Mn$_{0.5}$O$_3$ forms a single layer rather than a domain. Lithium-ion extraction from a single-layer Li$_{1.25}$Mn$_{2.5}$O$_4$ slab will induce fewer local structure changes than extraction from the domain, resulting in a lower Debye–Waller factor. Therefore, although the capacity contribution of the oxygen reduction is considerable, the O2-type material exhibits good cyclic stability (Figure S13, Supporting Information).

In situ XRD patterns were collected during the first charge, first discharge, second charge, and second discharge (Figure S14, Supporting Information). Before the voltage plateau is reached, the (002) peak shifts to a higher angle, reflecting a decrease in the lattice parameter c due to the decreased repulsion between the oxygen layers caused by the increase in the average metal–metal distance due to the oxidation of Co$^{2+}$ to Co$^{3+}$. Unlike O3-type materials, the intensity of the superstructure peaks during the first charge increases within the voltage plateau region (4.5–4.8 V) and then remains stable in the subsequent cycles. This suggests that the arrangement of the Li and Mn atoms in the transition-metal layer becomes more ordered and then remains stable. The evolution of the superstructure peaks also confirms that the Mn atoms do not migrate, resulting in a stable structure during cycling. This means the O2-type Li-rich materials can deliver a high reversible capacity without voltage fading.

In summary, the incorporation of the single-layer Li$_3$MnO$_3$ superstructure alters the oxygen redox process and leads to small structural changes during cycling. This can resolve issues resulting from the irreversible Li$_3$MnO$_3$ activation even with significant oxygen redox activity. The combination of the O2-type structure and single-layer Li$_3$MnO$_3$ superstructure endows the synthesized material with an extraordinary reversible capacity of 400 mAh g$^{-1}$. Our findings provide a new scope in designing high capacity cathode materials for the next generation of Li-ion batteries.

**Experimental Section**

**Synthesis of Samples:** The Co$_{0.26}$Mn$_{0.54}$(CO$_3$)$_{0.7}$ precursor was prepared using a coprecipitation method. An aqueous solution containing the required stoichiometric amounts of MnSO$_4$ (2.0 mol dm$^{-3}$, J&K, 99.99%), and CoSO$_4$ (2.0 mol dm$^{-3}$, J&K, 99.99%) was pumped into a 500 mL beaker with continuous stirring. An aqueous solution of Na$_2$CO$_3$ (2.0 mol dm$^{-3}$) with a controlled amount of NH$_4$OH as a chelating agent was simultaneously fed into the reactor. The temperature and pH of the solution were maintained at 50 °C and 7.5, respectively, throughout the coprecipitation reaction. The Co$_{0.26}$Mn$_{0.54}$(CO$_3$)$_{0.7}$ precipitate was filtered, washed, and dried in vacuum at 100 °C. This as-prepared CoMn carbonate precursor was thoroughly mixed with Na$_2$CO$_3$ and Li$_2$CO$_3$ at a molar ratio of Na$_2$Li:M = 10:8.3:9. Then, the mixture was calcined in air at 450 °C for 4 h and then at 800 °C for 8 h to form a black powder.

The compound, Na$_{2}$Li$_{1/3}$Mn$_{2/3}$O$_{2}$(M = Mn$_{0.67}$Co$_{0.33}$), was subjected to ion exchange in molten LiNO$_3$/LiCl (88:12 w/w) at 280 °C for 4 h. The chemical compositions of the as-prepared materials were determined by inductively coupled plasma optical emission spectroscopy analysis.

**Materials Characterization:** To investigate the crystal structure of the as-prepared materials, XRD was performed using a D8 Advance diffractometer (Bruker, Germany) with CuKα radiation (λ = 1.5406 Å) and operating at 40 kV and 40 mA. The scan data were collected in the 2θ range of 10°–80° with a step size of 0.02° and a counting time of 4 s. The morphology and structure analyses were performed using a JEOL JEM-ARM200F Dual-X transmission electron microscope at the Toray Research Center (Japan, Tokyo). The high X-ray absorption spectrum (XAS) Mn and Co K-edge spectra were collected in the fluorescence mode at beamline 1 W2B with a Si(111) double-crystal monochromator at the Beijing Synchrotron Radiation Facility (BSRF). To prepare the samples during the charging processes for ex situ measurements, all the cells were charged and discharged at a current density of 10 mA g$^{-1}$ and then disassembled in an Ar-filled glove box. The materials on Al foil were sealed with 3M tape (810-QC25) before being taken out of the glove box and packed into an Ar-filled bag. The energy calibration was carried out at the first inflection point of the Mn and Co foil, which was the reference (Mn K-edge = 6539 eV, Co K-edge = 7709 eV). An XAS data analysis was carried out according to the standard procedure with the IFEFFIT suite (1.2.11). The spectrum below the pre-edge region was fitted to a straight line, and then the post-edge background was subtracted based on the cubic spline procedure.

**Electrochemical Characterization:** The cathode electrode was prepared by placing a mixture of 80 wt% active material, 10 wt% Super P, and 10 wt% polyvinylidene fluoride (PVDF) onto Al foil. Before fabrication, the cathode electrode was dried at 120 °C overnight. The electrolyte was purchased from the Beijing Institute of Chemical Reagents, and a Whatman glass microfiber filter was used as the separator. The R2032-type coin cells used for the electrochemical testing were fabricated using Li metal as the anode in an Ar-filled glovebox with oxygen and moisture contents of less than 0.5 ppm. The galvanostatic charge–discharge process for all of the materials was measured by a Neware battery tester (5 V, 10 mA) at room temperature (25 °C).

**Calculation:** Calculation methods in this work were based on density functional theory (see Computational Details, Supporting Information).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.
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