A New Sealed Lithium-Peroxide Battery with a Co-Doped Li$_2$O Cathode in a Superconcentrated Lithium Bis(fluorosulfonyl)amide Electrolyte

Shin-ichi Okuoka$^1$, Yoshiyuki Ogasawara$^2$, Yosuke Suga$^2$, Mitsuhiro Hibino$^2$, Tetsuichi Kudo$^2$, Hironobu Ono$^2$, Koji Yonehara$^1$, Yasutaka Sumida$^1$, Yuki Yamada$^2$, Atsuo Yamada$^3$, Masaharu Oshima$^4$, Eita Tochigi$^5$, Naoya Shibata$^5$, Yuichi Ikuhara$^5$ & Noritaka Mizuno$^2$

$^1$Advanced Materials Research Center, Nippon Shokubai Co., Ltd. 5-8, Nishi Otabi-cho, Suita, Osaka, Japan, $^2$Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan, $^3$Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan, $^4$Synchrotron Radiation Research Organization, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan, $^5$Institute of Engineering Innovation, School of Engineering, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo, Japan.

We propose a new sealed battery operating on a redox reaction between an oxide (O$_2^{2-}$) and a peroxide (O$_2^{2-}$) with its theoretical specific energy of 2570 Wh kg$^{-1}$ (897 mAh g$^{-1}$, 2.87 V) and demonstrate that a Co-doped Li$_2$O cathode exhibits a reversible capacity over 190 mAh g$^{-1}$, a high rate capability, and a good cyclability with a superconcentrated lithium bis(fluorosulfonyl)amide electrolyte in acetonitrile. The reversible capacity is largely dominated by the O$_2^{2-}$/O$_2^{2-}$ redox reaction between oxide and peroxide with some contribution of the Co$^{2+}$/Co$^{3+}$ redox reaction.

Rechargeable lithium ion batteries (LIBs) operating on shuttling of lithium between the negative and positive electrodes, both of which are composed of topotactic insertion hosts of lithium such as graphite and LiCoO$_2$, are indispensable to our society as power sources for portable and large electronic appliances such as notebook computers and electric vehicles. However, their energy densities are rather modest; even the state-of-the-art LIBs do not exceed 250 Wh kg$^{-1}$. Therefore, various researches are being carried out to develop post-LIBs with much higher energy densities.

One of the approaches is utilization of electrode materials operating on so-called conversion reactions and the theoretical specific capacity is 714 mAh g$^{-1}$ for the reaction of CoO + 2Li$^+$ + 2e$^-$ → Co + Li$_2$O$^1$, while the severe hysteresis in voltage between the charging and discharging processes generally limits the energy efficiency. Moreover, some metal oxides including CoO show surprisingly good cycling reversibility despite the highly destructive nature of the conversion reaction. However, such oxide materials can be used only for anodes, because their working potentials are typically in the range of 0–1 V (vs. Li/Li$^+$) and low. Recently, some fluorides such as BiF$_3$ and FeF$_2$ (or FeF$_3$)$^2$ have been reported to operate at higher potentials (2.7–3.4 V), while their poor kinetics and reversibility are problems.

Another approach is a development of a lithium-air (Li-O$_2$) battery by use of atmospheric O$_2$ with a theoretical specific energy of 3400 Wh kg$^{-1}$ even including the weight of oxygen in the discharged product (Li$_2$O$_2$). However, the actual capacity or the energy is dependent on the pore volumes of the cathode matrices where Li$_2$O$_2$ is formed, the pores are clogged with solids, and the discharge is prohibited by the limitation of the oxygen supply. In addition, there are more serious inherent problems of the open device, suffering from the coexisting moisture and CO$_2$, and safety for the application to electronic vehicles. The main discharge product for Li-O$_2$ batteries is Li$_2$O$_2$ according to the reaction (the equilibrium potential, $E^*$ (vs. Li/Li$^+$))$^{4,5}$,

\[
O_2 + 2Li^+ + 2e^- \rightarrow Li_2O_2 \ (E_1 = 2.96 \ V).
\]

The subsequent reduction of Li$_2$O$_2$ has recently been pointed out to take place to form Li$_2$O during the deep discharge according to the reaction$^{6,9}$,
\[ \text{Li}_2\text{O} + 2\text{Li}^+ + 2e^- \rightarrow \text{2Li}_2\text{O} \quad (E_z = 2.87 \text{ V}) \].

However, there is no report on the repetition of the charge and discharge utilizing the reaction between Li\(_2\text{O}\) (or O\(^2-\)) and Li\(_2\text{O}_2\) (or O\(_2\)\(^2-\)). The investigation on LIB cathodes such as Li\(_2\text{CoO}_2\) and Li-rich layered oxides shows not only the charge compensation mechanism involving transition metal ions but also some contribution of the reversible redox reaction of oxygen atoms\(^{10-13}\). Therefore, we have reached an idea that Li\(_2\text{O}_2\) would act as a 3 V-level cathode utilizing the redox couple of oxide (O\(^2-\))/peroxide (O\(_2\)\(^2-\)) [equation (2)]. In addition, a certain electrode catalyst or mediator would selectively accelerate the thermodynamically more favourable backward reaction of equation (2) instead of the backward reaction of equation (1) and the following reaction:

\[ \text{Li}_2\text{O} \rightarrow 1/2\text{O}_2 + 2\text{Li}^+ + 2e^- \quad (E_z = 2.91 \text{ V}) \].

Here, we propose a new sealed battery operating on a redox reaction between O\(^2-\) and O\(_2\)\(^2-\) with its theoretical specific energy of 2570 Wh kg\(^{-1}\) (897 mAh g\(^{-1}\), 2.87 V, see the Supplementary Information) based on the reaction,

\[ 2\text{Li} + \text{Li}_2\text{O}_2 \rightarrow 2\text{Li}_2\text{O} \],

and demonstrate that a Co-doped Li\(_2\text{O}\) cathode exhibits a reversible capacity over 190 mAh g\(^{-1}\), a high rate capability, and a good cyclability with a superconcentrated lithium bis(fluorosulfonyl)amide (LiFSA) electrolyte in acetonitrile\(^8\). The reversible capacity is largely dominated by the reaction of equation (2) with some contribution of the redox reaction of Co ions.

**Results**

**Preparation and Characterization of the Co-Doped Li\(_2\text{O}\) Cathode.** The powders (Co/Li = 0.025–0.2) of Li\(_2\text{O}\) and Co\(_2\text{O}_4\) were pulverized and the Co-doped Li\(_2\text{O}\) were obtained. Among them, the Co-doped Li\(_2\text{O}\) (Co/Li = 0.1) showed the best charge-discharge performance (Supplementary Figure S1a). The electronic conductivity of the Co-doped Li\(_2\text{O}\) (Co/Li = 0.1) powder compact was \(5.3 \times 10^2\) k\(\Omega\) cm, while Li\(_2\text{O}\) is an insulator. Therefore, the resulting Co-doped Li\(_2\text{O}\) (Co/Li = 0.1) was hereafter used as a cathode and the specific capacity was calculated on the basis of the total weight of the Co-doped Li\(_2\text{O}\). Rh\(_2\text{O}_3\) and Ir\(_2\text{O}_3\) could also act similarly to Co\(_3\text{O}_4\) (Supplementary Figure S3). The absorption edge position agreed largely in the Co\(_2\text{O}_4\) (Supplementary Figure S1b).

In the X-ray diffraction (XRD) pattern of the Co-doped Li\(_2\text{O}\) (Supplementary Figure S2), broad peaks of anti-fluorite-type Li\(_2\text{O}\) and a weak peak at 44.8° of cubic LiCo\(_2\text{O}_4\)\(^{13}\) were observed, while peaks of spinel-type Co\(_2\text{O}_4\) were not observed. The peak intensity of the cubic LiCo\(_2\text{O}_4\) increased upon increase in the Co/Li ratio.

The Co K-edge X-ray absorption near edge structure (XANES) measurement of the Co-doped Li\(_2\text{O}\) was carried out to investigate the oxidation states and coordination environments of the Co species (Supplementary Figure S3). The absorption edge position agreed with that of starting Co\(_2\text{O}_4\), indicating that the average Co valence does not change under mechanical milling conditions. The pre-edge peak of the Co-doped Li\(_2\text{O}\) was stronger than those of Co\(_2\text{O}_4\) and LiCo\(_2\text{O}_4\) and as strong as that of the spinel CoAl\(_2\text{O}_4\), in which every Co\(^{2+}\) ion is located at the tetrahedral site. This absorption represents the transition of the 1s electron to an unoccupied d orbital of Co ions, which is an electric dipole forbidden transition in an ideal octahedral symmetry, while the noncentrosymmetric tetrahedral environment allows the transition\(^{14-17}\). Thus, the intense pre-edge peak shows the presence of considerable amounts of tetrahedral Co.

**Electrochemical Performance.** The charge and discharge curves of the cell consisting of the Co-doped Li\(_2\text{O}\) cathode, a Li metal anode, and a superconcentrated 4 M LiFSA electrolyte in acetonitrile\(^8\) are shown in Figure 1. The charge voltage gradually increased and reached approximately 3.2 V above 150 mAh g\(^{-1}\). The discharge and charge curves from the first to 15th cycle almost unchanged with the constant coulombic efficiency of ca. 96% at 45 mAh g\(^{-1}\) (Figure 1a). The 1st discharge capacity reached 195 mAh g\(^{-1}\) at a low current density of 13.5 mAh g\(^{-1}\) and the capacity of 133 mAh g\(^{-1}\) can be discharged even at a very high current density of 1080 mAh g\(^{-1}\) at which the capacity of 200 mAh g\(^{-1}\) can be charged in 11 min (Figure 1b).

**Peroxide Analysis in the Co-Doped Li\(_2\text{O}\) Cathode during the Charge and Discharge Process.** We quantified O\(_2\)\(^2-\) species in the Co-doped Li\(_2\text{O}\) cathode at various charge and discharge capacities. Figure 3a shows the amounts of the O\(_2\)\(^2-\) (detected as O\(_2\)) in the cathode at various charge capacities. In the range of 0–54 mAh g\(^{-1}\), the amounts of the O\(_2\)\(^2-\) were negligible. In the region 54–216 mAh g\(^{-1}\), the amounts of the O\(_2\)\(^2-\) increased and the slope from 162 mAh g\(^{-1}\) to 216 mAh g\(^{-1}\) corresponded to 0.5 O\(_2\)\(^2-\)/e\(^-\). In the final region of 216–270 mAh g\(^{-1}\), the amounts of the O\(_2\)\(^2-\) more gradually increased.

Figure 3d shows amounts of the O\(_2\)\(^2-\) in the cathode at various discharge capacities after the charge to 270 mAh g\(^{-1}\). In the region of 0–162 mAh g\(^{-1}\), the amounts of the O\(_2\)\(^2-\) decreased and the slope from 0 mAh g\(^{-1}\) to 108 mAh g\(^{-1}\) corresponded to 0.5 O\(_2\)\(^2-\)/e\(^-\). In the
Figure 2 | Co K-edge XANES spectra of the Co-doped Li$_2$O cathode at various charge and discharge capacities. The current densities were 4.5 mA g$^{-1}$. The insets show the absorption edge regions of the spectra. (a) Charge process. (b) Discharge process.

The final region of 162–250 mAh g$^{-1}$, the O$_2$$^{2-}$ was hardly detected. We also quantified the O$_2$$^{2-}$ species in the cathode recharged to 270 mAh g$^{-1}$. The amount of the O$_2$$^{2-}$ was 2.31 mmol g$^{-1}$ in approximate agreement with that for the first charge.

**Observation and Analysis of the Cathode during the Charge.** The in-situ gas phase analysis during the charge process was conducted. In Figure 4b, cumulative amounts (per weight of the Co-doped Li$_2$O cathode) of O$_2$ and CO$_2$ evolved are shown together with its charge curve (Figure 4a). In the range of 0–216 mAh g$^{-1}$, O$_2$ was hardly observed, and then the amount of O$_2$ evolution monotonically increased. The slope of O$_2$ evolution in the range of 324–594 mAh g$^{-1}$ almost corresponded to 0.25 O$_2$/e$^-$. The XRD 111 peak intensity of the Co-doped Li$_2$O was approximately linearly weakened with increase in the charge capacity from 0 to 324 mAh g$^{-1}$ and was more slowly weakened at 540 and 580 mAh g$^{-1}$ (Figure 4c and

Figure 3 | Analysis of the Co-doped Li$_2$O cathodes after the charge and the discharge. (a) and (d) Analytical peroxide amounts of the cathodes after the charge (a) and discharge (d). (b) and (e) Co K-edge XANES absorption edge positions of the cathodes after the charge (b) and discharge (e). (c) and (f) Charge (c) and discharge (f) voltage curves at current density of 4.5 mA g$^{-1}$. 

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Figure 4 | Voltage, gas evolution, XRD peak intensity of the Co-doped Li$_2$O cathode in the charge process. (a) The voltage curve. (b) Cumulative amounts of O$_2$ and CO$_2$ evolved in the charge process at the current density of 4.5 mA g$^{-1}$. The slope of 0.25 O$_2$/e$^-$ indicates theoretical rate of O$_2$ evolution according to the reaction, 2O$_2$ $\rightarrow$ 4e$^-$. (c) The XRD 111 peak intensity of Co-doped Li$_2$O. The peak intensity at 0 mAh g$^{-1}$ was taken as a unity. The black line is a theoretical line of change in the peak intensity.

Supplementary Figure S4). The evolution of CO$_2$ was not observed in the whole range of the charge process.

Direct observation of the Co-doped Li$_2$O cathode charged to 270 mAh g$^{-1}$ was attempted with high resolution transmission electron microscopy (HRTEM). Figure 5 shows the HRTEM image and the fast Fourier transform (FFT) pattern. Since some spots in Figure 5b lie on the circles estimated with the Li$_2$O$_2$ crystal structure, many fringe regions surrounded by red circles in Figure 5a are likely attributable to Li$_2$O$_2$. In contrast, for the starting cathode before the charge, since all spots (Supplementary Figure S5b) lie on the circles estimated with Li$_2$O or cubic LiCoO$_2$ crystal structures, many fringe regions surrounded by red circles (Supplementary Figure S5a) are likely attributable to Li$_2$O or cubic LiCoO$_2$.

Discussion

Upon increase in Co content above Co/Li = 0.1, the discharge capacity decreased (Supplementary Figure S1a) and the XRD peak intensity of cubic LiCoO$_2$ increased (Supplementary Figure S2), suggesting that the resulting cubic LiCoO$_2$ is inactive for the charge and discharge reactions at the voltage of 2.0–3.2 V (vs. Li/Li$^+$) as has been reported in ref. (18).

In the XRD pattern of the Co-doped Li$_2$O (Supplementary Figure S2), broad peaks of anti-fluorite-type Li$_2$O and a weak peak at 44.8$^\circ$ of cubic LiCoO$_2$ were observed, while peaks of spinel-type Co$_3$O$_4$ were not observed. The volume fractions of Co-doped Li$_2$O and cubic LiCoO$_2$ were estimated to be 0.90:0.10 with the parameters of 111 reflection of Co-doped Li$_2$O and 200 one of cubic LiCoO$_2$ in Supplementary Table S1 (see the Supplementary Information). The Co K-edge XANES spectrum of the Co-doped Li$_2$O shows the presence of considerable amounts of tetrahedral Co (Supplementary Figure S3). These results indicate that most of Co ions are substitutionally doped in the tetrahedral Li sites of the anti-fluorite Li$_2$O structure with formation of vacancies at the same sites due to charge compensation. Co$^{2+}$ and Co$^{3+}$ in the Co-doped Li$_2$O would be randomly distributed at the tetrahedral sites in a defective anti-fluorite structure, since the XRD pattern was not identical to that of the defective anti-fluorite structure, in which Co ions were ordered in the tetrahedral sites.

The Co-doped Li$_2$O cathode, of which the theoretical specific capacity is calculated to be 556 mAh g$^{-1}$ based on the weight of Li$_2$O in the Co-doped Li$_2$O (see the Supplementary Information), exhibited a reversible capacity over 190 mAh g$^{-1}$, a high rate capability, and a good cyclability (Figure 1). The electronic conductivity of the Co-doped Li$_2$O powder compact was $5.3 \times 10^{-2}$ kΩ cm and of the same level ($5 \times 10^{-2}$ kΩ cm) as that of LiMn$_2$O$_4$ $^{21}$, showing that the Co-doped Li$_2$O can work as an electrode material. This conductivity is possibly explained by narrowing of the Li$_2$O band gap by formation of the impurity state with the dope of Co or becoming metallic by the carrier dope. The coulombic efficiency of the present system is 96% and still below 100%. This is possibly explained by the progress of the side reaction of solid electrolyte interface formation during the charge other than CO$_2$ formation.

To clarify the oxidation states of Co and the presence of O$_2^{2-}$ in the Co-doped Li$_2$O cathode, the Co K-edge XANES measurement and
quantification of $O_2^{2-}$ species were carried out at various charge and discharge capacities (Figures 2 and 3). In the charge process from 0 to 54 mAh g$^{-1}$, the oxidation of Co$^{2+}$ to Co$^{3+}$ proceeds without the $O^2-$ oxidation (Figures 3a and 3b). The oxidation of Co$^{2+}$ to Co$^{3+}$ in the charge process is completed at the charge capacity $\leq$54 mAh g$^{-1}$ in accord with the theoretical capacity (39 mAh g$^{-1}$) of the cathode due to the oxidation of Co$^{2+}$ to Co$^{3+}$. In the region of 54–216 mAh g$^{-1}$, the amounts of the O$_2^{-}$ increased and the slope from 162 mAh g$^{-1}$ to 216 mAh g$^{-1}$ corresponded to 0.5 O$_2^{-}$/e$^-$, suggesting the O$_2^{-}$ formation according to the backward reaction of equation (2) (Figure 3a). In the final region of 216–270 mAh g$^{-1}$, the amounts of the O$_2^{-}$ more gradually increased. Considering the O$_2$ evolution curve (Figure 4b), both the O$_2^{-}$ formation and O$_2$ evolution reactions likely proceed in this region.

In the discharge process from 0 to 162 mAh g$^{-1}$, the amounts of the O$_2^{-}$ decreased and the slope from 0 mAh g$^{-1}$ to 108 mAh g$^{-1}$ corresponded to 0.5 O$_2^{-}$/e$^-$, suggesting the consumption of the O$_2^{-}$ according to equation (2) (Figure 3d). In the final region of 162–250 mAh g$^{-1}$, the O$_2^{-}$ was hardly detected, indicating that the discharge mostly consists of the reduction of Co$^{3+}$ to Co$^{2+}$, in agreement with the Co K-edge XANES results (Figures 2b and 3e). In the recharge process to 270 mAh g$^{-1}$, the amount of the O$_2^{-}$ was 2.31 mmol g$^{-1}$ in approximate agreement with that for the first charge, suggesting reversible formation of O$_2^{-}$ in the repeated cycles.

It is essentially important for the present battery that no substantial amount of O$_2$ is released in the charge process. Moreover, CO$_2$ evolution accompanied by anodic side reactions between Li$_2$O$_2$ and carbon additives or electrolytes has been pointed out as a problem of the Li$_2$O$_2$ batteries$^{22-24}$. In the range of 0–216 mAh g$^{-1}$, O$_2$ was hardly observed (Figure 4b), suggesting that the side reactions of O$_2$ evolution do not proceed and Co-doped Li$_2$O$_2$ is oxidized according to the reaction, 2O$^{-} \rightarrow$ O$_2$ + 2e$^-$, with some contribution of the oxidation of Co ions. The slope of 0.25 O$_2^{-}$/e$^-$ in the range of 324–594 mAh g$^{-1}$ suggests that O$_2$ is formed according to the direct reaction (i) 2Li$_2$O$\rightarrow$ O$_2$ + 4Li$^+$ + 4e$^-$ and/or the consecutive reaction (ii) 2Li$_2$O$\rightarrow$ Li$_2$O$_2$ + 2Li$^+$ + 2e$^- \rightarrow$ O$_2$ + 4Li$^+$ + 4e$^-$ (the overall reaction, 2O$^{-} \rightarrow$ O$_2$ + 4e$^-$). The investigation on the mechanism of the O$_2$ evolution is in progress. The XRD 111 peak intensity of the Co-doped Li$_2$O$_2$ was approximately linearly weakened with increase in the charge capacity toward the theoretical capacity of 556 mAh g$^{-1}$ (Figure 4c and Supplementary Figure S4). The upper deviation from the linear line at 540 and 580 mAh g$^{-1}$ is probably due to the O$_2$ evolution. While the HRTEM image shows fringe regions attributed to Li$_2$O$_2$ (Figure 5), the XRD patterns of Co-doped Li$_2$O$_2$ upon charged to 270, 324 and 540 mAh g$^{-1}$ showed no Li$_2$O$_2$ signal (Supplementary Figure S4) because of the small amount and poor crystallinity. The evolution of CO$_2$ was not observed in the whole range of the charge process, showing that the Co-doped Li$_2$O$_2$ cathode is free from side reactions to produce CO$_2$ and the superconcentrated LiFSA electrolyte in acetonitrile is stable under the present conditions.

All results demonstrate that the Co-doped Li$_2$O$_2$ cathode is charged without the O$_2$ evolution in the region of 0–216 mAh g$^{-1}$ (Figure 4b) via the oxidation of Co$^{2+}$ to Co$^{3+}$ (0–54 mAh g$^{-1}$) (Figure 2a) and the subsequent oxidation of O$^2-$ to O$_2$ (54–216 mAh g$^{-1}$) (Figure 3a) according to the reaction, 2Li$_2$O$\rightarrow$ Li$_2$O$_2$ + 2Li$^+$ + 2e$^-$: $E = 2.87$ V. In the higher capacity range, O$_2$ was evolved, suggesting the progress of reactions with the higher equilibrium potential, 2Li$_2$O$\rightarrow$ O$_2$ + 4Li$^+$ + 4e$^-$: $E = 2.91$ V and/or Li$_2$O$_2$ $\rightarrow$ O$_2$ + 2Li$^+$ + 2e$^-$: $E = 2.96$ V as expected thermodynamically. At the present stage, the reversible specific capacity of the Co-doped Li$_2$O$_2$ cathode was ca. 200 mAh g$^{-1}$ and lower than its theoretical 556 mAh g$^{-1}$.

In conclusion, we have proposed and demonstrated a new sealed and high-rate battery operating on a redox reaction between O$^2-$ and O$_2^-$.
under vacuum. Then, the sample, 1 g of ice water in a small glass container frozen with liquid nitrogen at 77 K, and a small amount of Pt powder (< 1 mg) were put into the beaker cell (Supplementary Figure S6) and the beaker cell was closed with a gas tight glass cap. The resulting beaker cell, a circulation cylinder, and a 2-position 6-port valve with a sampling loop were assembled. All these procedures were carried out in an Ar-filled glove box. Then, the system was quickly transferred outside and connected to the gas flow system directly connected to a quadrupole mass spectrometer (OmniStar GSD301, Pfeiffer Vacuum) (Supplementary Figure S6). Before the ice melted, the background oxygen concentration in the cell was analysed with an oxygen spectrometer (Supplementary Figure S6).

1. Poizot, P., Laruelle, S., Grugel, S., Dupont, L. & Tarascon, J.-M. Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries. Nat. Mater. 407, 496–499 (2000).

2. Bervas, M. et al. Investigation of the lihiation and delithiation conversion mechanisms of bismuth fluoride nanocomposites. J. Electrochem. Soc. 153, A799–A808 (2006).

3. Badway, F., Pereira, N., Cosandey, F. & Amatucci, G. G. Carbon-metal fluoride nanocomposites structure and electrochemistry of FeF2:C. J. Electrochem. Soc. 150, A1209–A1218 (2003).

4. Abraham, K. M. & Jiang, Z. A polymer electrolyte-based rechargeable lithium/oxygen battery. J. Electrochem. Soc. 143, 1–5 (1996).

5. Ogasawara, T., Débart, A., Holzapfel, M., Novák, P. & Bruce, P. G. Rechargeable Li2O2 electrode for lithium batteries. J. Am. Chem. Soc. 128, 1390–1393 (2006).

6. Zhang, S. S., Foster, D. & Read, J. Discharge characteristic of a non-aqueous LiO2-MnO2 cathode for lithium secondary batteries. J. Power Sources 196, 1241–1247 (2011).

7. Thapa, A. K. & Ishihara, T. Mesoporous α-MnO2/Pd catalyst air electrode for rechargeable lithium–air battery. J. Power Sources 196, 7016–7020 (2011).

8. Trahan, M. J. et al. Cobalt philonolycanite catalyzed lithium-air batteries. J. Electrochem. Soc. 160, A1577–A1586 (2013).

9. Sathiya, M. et al. Reversible anodic redox chemistry in high-capacity layered-oxide electrodes. Nat. Mater. 12, 827–835 (2013).

10. Sathiya, M. et al. High performance Li-Ru yMnO2 (0.2 ≤ y ≤ 0.8) cathode materials for rechargeable lithium-ion batteries: Their understanding. Chem. Mater. 25, 1121–1131 (2013).

11. Koga, H. et al. Different oxygen redox participation for bulk and surface: A possible global explanation for the cycling mechanism of Li1.2yMn1.8O4 and Li1.5FeO4, J. Power Sources 236, 250–258 (2013).

12. Yoon, W. et al. Oxygen contribution on Li-ion intercalation-deintercalation in LiCoO2 investigated by O K-edge and Co L-edge X-ray absorption spectroscopy. J. Phys. Chem. B 106, 2526–2532 (2002).

13. Yamada, Y. et al. Unusual stability of acetonitrile-based superconcentrated electrolytes for fast-charging lithium-ion batteries. J. Am. Chem. Soc. 136, 5039–5046 (2014).