A lithium–oxygen battery based on lithium superoxide

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Batteries based on sodium superoxide and on potassium superoxide have recently been reported1–3. However, there have been no reports of a battery based on lithium superoxide (LiO2), despite much research4–8 into the lithium–oxygen (Li–O2) battery because of its potential high energy density. Several studies9–16 of Li–O2 batteries have found evidence of LiO2 being formed as one component of the discharge product along with lithium peroxide (Li2O2). In addition, theoretical calculations have indicated that some forms of LiO2 may be thermodynamically unstable with respect to disproportionation, giving Li2O2 (refs 19, 20). Here we show that crystalline LiO2 can be stabilized in a Li–O2 battery by using a suitable graphene-based cathode. Various characterization techniques reveal no evidence for the presence of Li2O2. A novel templating growth mechanism involving the use of iridium nanoparticles on the cathode surface may be responsible for the growth of crystalline LiO2. Our results demonstrate that the LiO2 formed in the Li–O2 battery is stable enough for the battery to be repeatedly charged and discharged with a very low charge potential (about 3.2 volts). We anticipate that this discovery will lead to methods of synthesizing and stabilizing LiO2, which could open the way to high-energy-density batteries based on LiO2 as well as to other possible uses of this compound, such as oxygen storage.

The crystalline LiO2 reported here was made electrochemically using a cathode based on reduced graphene oxide (rGO) with added iridium (Ir) nanoparticles. Initially graphene oxide (GO) was prepared by a modified Hummer’s method21,22. The Ir–rGO composite was then made by a hydrothermal reduction method and characterized (Supplementary Fig. 2). Scanning electron microscopy (SEM) images (Supplementary Fig. 3) of the pristine rGO and Ir–rGO composite (Fig. 1a and b, respectively) reveal porous three-dimensional (3D) networks of rGO composed of wrinkled 2D rGO sheets. Figure 1c and d shows transmission electron microscopy (TEM) images of the Ir nanoparticles on rGO, indicating that the well-dispersed Ir nanoparticles decorated on rGO are very small (< 2 nm), with evidence for the presence of some small Ir clusters (circled in Fig. 1d). A backscattering image (Supplementary Fig. 1) shows some scattered larger Ir particles of about 500 nm in size, which may be due to agglomeration of the smaller nanoparticles, and fast Fourier transform analysis of high-resolution (HR)-TEM images (Supplementary Fig. 1) show that the nanoparticles are Ir. An X-ray photoemission spectroscopy (XPS) analysis (Supplementary Fig. 1) indicates the Ir surface is only partially oxidized.

The performance of the rGO and Ir–rGO cathodes was examined using a Swagelok-type cell composed of a lithium metal anode, electrolyte (1 M LiCF3SO3 in tetraethylene glycol dimethyl ether (TEGDME)) impregnated into a glass fibre separator, and a porous cathode. A current density of 100 mA g−1 was used for both discharge and charge, and the cell was run with a capacity limit of 1,000 mAh g−1 to avoid side reactions. The specific capacity (mAh g−1) and the current density (mAg−1) are based on the active materials of the O2 electrodes. Figure 2a and b shows voltage profiles for the Ir–rGO and rGO cathode architectures, respectively. The Ir–rGO discharge product shows a very low charge potential of ~3.2 V that rises to 3.5 V over 40 cycles leading to more than 85% efficiency in this system (Fig. 2a). The voltage profile of the rGO cathode shows a much larger charge potential of ~4.2 V with a lower efficiency of ~67% (Fig. 2b).

The discharge product resulting from the Ir–rGO cathode was examined using SEM, differential electrochemical mass spectroscopy (DEMS), high-energy X-ray diffraction (HE-XRD), TEM and Raman spectroscopy with the results shown in Figs 2 and 3. The SEM image (in Fig. 2c) shows the Ir–rGO cathode after discharge (~2.75 V) from the first cycle (1,000 mAh g−1 capacity). This image indicates that the discharge product resulting from the Ir–rGO-based cathode consists mainly of nanoparticles with needle- or rod-like morphology, although the presence of other shapes such as cubic cannot be ruled out. This needle- or rod-like morphology is also observed in the TEM image of a part of the discharge product, which appears to be on the surface of the Ir–rGO nanostructures (Fig. 2c inset). An SEM image after charging shows that the nanoparticles have disappeared (Supplementary Fig. 3). The discharge product from the rGO-based cathode has a range of morphologies, including toroids and nanoparticles (Supplementary Fig. 3). The Ir–rGO discharge product produced by a current density of 100 mA g−1 was characterized by DEMS during the first charging cycle by on-line monitoring of the number of evolved O2 molecules. The experiment was performed using high current densities (1,000 mAh g−1 and 640 mA g−1) for charging to enable measurement of the evolved O2. The DEMS results at the higher current density are shown in Fig. 2d. Analysis of the data in Fig. 2dg gives an average O2 formation rate of 1.3 × 10−9 mol s−1, resulting in an e−/O2 ratio of 1.0. A similar (1.00) e−/O2 ratio was also obtained for the experiment with a current density of 640 mA g−1 (Supplementary Fig. 18). Additionally, negligible amounts of CO2 and H2 gases were generated during the DEMS experiments (Fig. 2d and Supplementary Fig. 18). A DEMS experiment was also carried out during discharge, and gave an e−/O2 ratio of 1.02 (Supplementary Fig. 18, Supplementary Table 3). These results are consistent with Li2O2 as the main discharge product, and provide evidence for the absence of other products (for example, Li2O3, LiOH and Li2CO3). The DEMS results for Li2O2 are similar to DEMS measurements on a Na2O battery that gave an e−/O2 ratio of 1.00 for discharge and 1.02 for charge4.

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Figure 1 | Morphology of Ir–rGO. a, SEM image of pristine rGO powder. b, SEM image of Ir–rGO composite. c, d, TEM images of Ir–rGO composite, showing Ir nanoparticles less than 2 nm in size. The circle in d shows some small Ir atomic clusters. Scale bars: a, b, 1 μm; c, 10 nm; d, 2 nm. There are also some scattered large Ir agglomerates on the rGO (see Supplementary Fig. 1).

Figure 2 | Electrochemical tests and discharge products. a, Voltage profiles of the Ir–rGO cathode (see also Supplementary Fig. 6). Cycle number of voltage plot is given by the colour of the plotting symbol (see key). Inset shows capacity as a function of cycle number. b, Voltage profiles of the rGO cathode. Cycle number of voltage plot is given by the colour of the plotting symbol (see key). Inset shows capacity as a function of cycle number. c, Main panel, SEM image of discharge product on Ir–rGO (scale bar, 1 μm); inset, TEM image of discharge product on Ir–rGO (scale bar, 200 nm). Both main panel and inset are from the first discharge with a current density of 100 mA g⁻¹, and capacity control of 1,000 mAh g⁻¹. d, DEMS profile showing O₂, H₂ and CO₂ gases released (∗ is the number of moles per second) from the cell during the charging process (at 1,000 mA g⁻¹ current density) after the first discharge (at 100 mA g⁻¹ current density) to 1,000 mA h g⁻¹ capacity (see Supplementary Information for details).
The HE-XRD pattern in Fig. 3a for the discharge product on the Ir-rGO cathode (1,000 mA h g\(^{-1}\)) capacity during the first cycle shows peaks corresponding to crystalline LiO\(_2\) ((101), (111), (120)), and no evidence for peaks corresponding to Li\(_2\)O\(_2\). The identification of the LiO\(_2\) peaks is based on a theoretical XRD pattern derived from the DFT (density functional theory)-predicted crystalline LiO\(_2\) structure (Supplementary Fig 4) from refs 19 and 23, as no experimental XRD pattern has been reported. The LiO\(_2\) structure is orthorhombic (Supplementary Fig. 4). For comparison, NaO\(_2\) is cubic at room temperature and orthorhombic at <196 K, whereas KO\(_2\) is tetragonal at room temperature. Some amorphous LiO\(_2\) cannot be ruled out on the basis of the XRD results. The standard XRD pattern of Li\(_2\)O\(_2\) was used to determine the absence of Li\(_2\)O\(_2\). The Raman spectra of the discharge product of the Ir-rGO cathode in Fig. 3b show the presence of a peak at 1,123 cm\(^{-1}\), consistent with the range of values that have been observed for superoxide stretching frequencies (Supplementary Table 1). It is also consistent with the Raman peak at 1,156 cm\(^{-1}\) observed\(^{1}\) for NaO\(_2\). There is also a peak at 1,505 cm\(^{-1}\) that has recently been attributed to the strong interaction between LiO\(_2\) and a graphitic carbon surface\(^9\). In contrast, the HE-XRD pattern that has recently been attributed to the strong interaction between LiO\(_2\) and a graphitic carbon surface\(^9\). In contrast, the HE-XRD pattern that has recently been attributed to the strong interaction between LiO\(_2\) and a graphitic carbon surface\(^9\).

Further evidence that the discharge product is LiO\(_2\) on the Ir-rGO cathode was obtained by an experiment in which Li was electrochemically added to the discharge product without the presence of O\(_2\) (that was, O\(_2\) was replaced by Ar). The voltage profile is shown in Fig. 3c for this discharge process, along with that of the initial discharge process (to 1,000 mA h\(^{-1}\)). The HE-XRD of the resulting product with no O\(_2\) in the cell is shown in Fig. 3d and reveals strong peaks from Li\(_2\)O\(_2\), thus indicating a conversion of LiO\(_2\) to Li\(_2\)O\(_2\) (Li\(^{+}\) + e\(^{−}\) + LiO\(_2\) → Li\(_2\)O\(_2\)) with ~96% of the theoretical capacity for this reaction attained. This is evidence for a reaction involving one electron per O\(_2\) in the first cycle for 1,000 mA h\(^{-1}\) capacity, and for no crystalline or amorphous Li\(_2\)O\(_2\) forming on the initial capacity-limited discharge. In contrast, no significant capacity for discharge in Ar is observed for the rGO cathode when a similar procedure is performed. We have also carried

Figure 3 | Characterization of discharge products. a, HE-XRD patterns of discharge product on Ir–rGO as a function of age time. b, Raman spectra of discharge product on Ir–rGO for first and second discharges. c, Voltage plots for Ir–rGO discharged first in O\(_2\) to a capacity of 1,000 mA h g\(^{-1}\) and then discharged in Ar during which time it attained a capacity 956 mA h g\(^{-1}\); in the latter case, the electrolyte was purged with Ar before discharge (see Supplementary Fig. 16 for comparison with other cathode materials). d, HE-XRD pattern of cathode resulting from both discharges in c. e–g, TEM image of an Ir agglomerate after first discharge (e; scale bar, 200 nm); f, HR-TEM image of boxed area in e (scale bar, 2 nm); and g, the corresponding electron diffraction pattern along the [100] zone axis giving evidence for the formation of an Ir\(_3\)Li intermetallic. The indices are diffraction vectors. Weak superstructure is observed as indicated by arrows.
The HE-XRD finding that rGO results in both LiO$_2$ and Li$_2$O$_2$ in the presence of oxygen. B, DFT calculations of the barrier for desorption ($\Delta E_{\text{act}}$) of an O$_2$ molecule from the (101)LiO$_2$ surface in vacuum from a Nudged Elastic Band (NEB) calculation as a function of number of reaction steps, N. C, AIMD simulations of (111)LiO$_2$ and (101)LiO$_2$ surfaces in vacuum at room temperature. D, DFT calculations of the barrier for desorption of an O$_2$ molecule from an amorphous LiO$_2$ surface in vacuum. E, DFT electronic band structure (left) and density of states (DOS) plot (right) of ferromagnetic bulk crystalline LiO$_2$ close to the Fermi level ($E_F$) based on a spin polarized calculation with electronic spin-up and spin-down states shown. (See also Supplementary Fig. 17.)

An explanation of the formation mechanism and stability of the LiO$_2$ found in this study requires an understanding of the growth and nucleation process, which is quite complex and beyond the scope of the present study. However, our results are consistent with mechanisms proposed in other recent studies. Some insight can be obtained from a postulated mechanism for the nucleation and growth of discharge products from various size-specific Ag clusters decorating carbon cathodes in a Li–O$_2$ cell. In that case, the results are explained by a through-solution growth mechanism with sites for oxygen reduction reactions (ORRs) that are separate from the nucleation sites. Other researchers have also reported evidence for through-solution mechanisms. In addition, the results of the Ag cluster study suggest that availability of good ORR sites promotes a through-solution mechanism involving nucleation and growth of LiO$_2$ followed by disproportionation to Li$_2$O$_2$. Since both Ir and rGO are good ORR materials, the Ir–rGO-based cathodes of the present study should result in a similar mechanism, that is, initial formation of LiO$_2$.

The HE-XRD finding that rGO results in both LiO$_2$ and Li$_2$O$_2$ in the discharge product can be accounted for by slow disproportionation. This explanation is supported by a recent theoretical study that has...
shown the possibility of fast and slow disproportionation processes for LiO₂ depending on the LiO₂ cluster size. In addition, experimental evidence for slow disproportionation has been found in studies of Li–O₂ cell discharge products based on an activated carbon cathode. In contrast, the present HE-XRD results showing that only LiO₂ is present in the case of the Ir–rGO-based cathode material suggest that disproportionation is suppressed.

The formation of only LiO₂ in the case of the present Ir–rGO cathode may be due to some aspect of that cathode that favours nucleation and growth of largely the crystalline LiO₂ phase, which prevents disproportionation (see theoretical calculations below). In the case of Ir–rGO, we noticed the formation of an Ir₃Li intermetallic compound on the large Ir agglomerates seen in the backscattering image (Supplementary Fig. 1), as shown Fig. 3f and g). We also noticed that some nanoparticles (needle or rod-like) are formed on the surface of these agglomerates during the first discharge (Fig. 3e). We note that the Ir₃Li intermetallic compound has an orthorhombic lattice, a similar crystallographic lattice to that of LiO₂. It is possible that it may act as a template for growth of the crystalline LiO₂, as has been found in template-controlled nucleation and growth of other crystalline materials. We carried out DFT calculations on the interface between LiO₂ and Ir₃Li, and found that some crystalline faces had good lattice matches (Supplementary Fig. 13), as would be required for epitaxial growth of crystalline LiO₂. There may be other intermetallic compounds that exhibit similar behaviour and will be the subject of further study. The schematic in Fig. 4 summarizes the novel templating process that may be responsible for the LiO₂ discharge product found for the Ir–rGO cathode material and the subsequent electrochemical reactions that it can undergo, that is, either further lithiation or further oxygen reduction. In contrast, the rGO cathode, which does not include Ir nanoparticles, probably has a different nucleation and growth mechanism resulting in a discharge product composed of both LiO₂ and Li₂O₂.

The kinetic stability of crystalline and amorphous LiO₂ was investigated using ab initio molecular dynamics (AIMD) and DFT calculations with the results shown in Fig. 4. The disproportionation rate will depend on several factors. One factor is the rate at which the O₂ leaves the surface. The DFT results in Fig. 4b indicate that the initial step of O₂ leaving the crystalline surface into vacuum has a barrier of ~0.9 eV based on a low-energy LiO₂ surface. Figure 4c shows that crystalline LiO₂ surfaces (that is, (101) and (111)) are thermally stable in vacuum at room temperature. For an amorphous surface, the barrier (~0.3 eV) is less than for the crystalline surface (Fig. 4d). From AIMD simulations, the presence of some solvent molecules adsorbed on the amorphous LiO₂ surface reduces O₂ desorption (Supplementary Fig. 14). This suggests that solvent on the LiO₂ surface could further suppress disproportionation of the crystalline phase. The electrolyte effect on disproportionation was investigated by allowing a sample from a 1,000 mA h g⁻¹ discharge to age for 24 h in vacuum. Characterization of the sample by Raman spectroscopy, discharge in Ar, and charge potential shows a significant decrease of LiO₂ signature after ageing in vacuum, indicating that kinetics plays an important role in stabilizing the LiO₂ (Supplementary Fig. 15).

The Ir–rGO cathode also exhibits a low charge potential, which may be due to several factors. As shown in Fig. 4e, crystalline LiO₂ is a half-metal (on the basis of density functional calculations) and, thus, will have good electronic conduction, in contrast to insulating bulk Li₂O₂. Another factor is that Ir is known to be a good oxygen evolution catalyst and interacts strongly with LiO₂ to form a good interface for electrical contact. These properties may explain why the discharge product formed on just rGO has a large charge potential, that is, it lacks the Ir nanoparticles. The Li–O₂ cell based on Ir–rGO cathode material also can cycle 40 or more times (Supplementary Fig. 9) before failure, similar to what has been found for Li₂O₃-based Li–O₂ cells, indicating that the lithium superoxide is not any more reactive towards the electrolyte than lithium peroxide. In addition, the low charge potential will lead to less side reactions. The failure of the cell could be due to oxygen crossover to the anode resulting in the anode being converted to LiOH, as evidenced by the corrosion of the anode (Supplementary Fig. 10) and, possibly the poisoning of Ir metal catalyst with cycling. When the cycled Li anode is replaced by a new anode, the cell cycles another 30 times (Supplementary Fig. 10).

The evidence presented here indicates that a Li–O₂ electrochemical cell based on a LiO₂ discharge product is possible with a reasonable cycle life, very high efficiency, and a good capacity. The performance characteristics of the cell based on LiO₂ are comparable to those of previously reported electrochemical cells based on KO₂ (ref. 3) and on NaO₂ (ref. 1), although some aspects—such as the charge and discharge potentials—differ. Problems with electrolyte stability and decomposition, as for the electrolytes used for other Li–O₂ systems, probably still remain, but they do not seem any worse than for those systems. There is little evidence of any side reactions in the Raman data for the first discharge cycle (Fig. 3b), or from Raman and Fourier transform infrared data after charging for up to 30 cycles (Supplementary Figs 11, 12), or from NMR data up to 20 cycles (Supplementary Fig. 12), although there could be decomposition products that are not detected. The Fourier transform infrared and Raman results also confirm that the discharge product is not present after charging.

In summary, we have reported evidence it is possible to have a one-electron discharge process that forms only LiO₂ in a Li–O₂ electrochemical cell. This is different from the previous studies that have provided evidence for both LiO₂ and Li₂O₂ in the discharge product of Li–O₂ batteries with some cathode and electrolyte materials, and from studies that have shown LiO₂ can be present in solution during discharge. The evidence for the existence of the LiO₂ comes from DEMS and HE-XRD data with no evidence for Li₂O₂ being present. The results of TEM and density functional calculations indicate that a novel templating growth mechanism involving the use of Ir nanoparticles may be responsible for the crystalline LiO₂ growth. The LiO₂ formed in this way is stable enough to be repeatedly charged and discharged with a very low charge overpotential.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

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1. Hartmann, P. et al. A rechargeable room-temperature sodium superoxide (NaO₂) battery. Nature Mater. 12, 228–232 (2013).
2. Hartmann, P. et al. A comprehensive study on the cell chemistry of the sodium superoxide (NaO₂) battery. Phys. Chem. Chem. Phys. 15, 11661–11672 (2013).
3. Ren, X. & Wu, Y. A low-overpotential potassium–oxygen battery based on potassium superoxide. J. Am. Chem. Soc. 135, 2923–2926 (2013).
4. Lu, J. et al. A nanostructured cathode architecture for low charge overpotential in lithium-oxygen batteries. Nature Commun. 4, 2383 (2013).
5. Bruce, P. G., Freunberger, S. A., Hardwick, L. J. & Tanascon, J.-M. LiO₂ and LiS batteries with high energy storage. Nature Mater. 11, 19–29 (2011).
6. Lu, J. et al. Aprotic and aqueous LiO₂ batteries. Chem. Rev. 114, 5611–5640 (2014).
7. Lu, J. et al. Effect of the size-selective silver clusters on lithium peroxide morphology in lithium–oxygen batteries. Nature Commun. 5, 4895 (2014).
8. Black, R., Lee, J.-H., Adams, B., Mims, C. A. & Nazar, L. F. The role of catalysts and peroxide oxidation in lithium–oxygen batteries. Angew. Chem. Int. Edn 52, 392–396 (2013).
9. Zhai, D. et al. Raman evidence for late stage disproportionation in a Li–O₂ battery. J. Phys. Chem. Lett. 5, 2705–2710 (2014).
10. Zhai, D. et al. Disproportionation in Li–O₂ batteries based on a large surface area carbon cathode. J. Am. Chem. Soc. 135, 15364–15372 (2013).
11. Yang, J. et al. Evidence for lithium superoxide-like species in the discharge product of a LiO₂ battery. Phys. Chem. Chem. Phys. 15, 3764–3771 (2013).
12. Gittleson, F. S., Ryu, W.-H. & Taylor, A. D. Operando observation of the gold-electrolyte interface in Li₂O₂ batteries. ACS Appl. Mater. Interfaces 6, 19017–19025 (2014).
13. Gittleson, F. S. et al. Raman spectroscopy in lithium-oxygen battery systems. ChemElectroChem 2, 1446–1457 (2015).
14. Olivares-Marin, M. et al. Spatial distributions of discharged products of lithium-oxygen batteries revealed by synchrotron X-ray transmission microscopy. Nano Lett. 15, 6932–6938 (2015).

15. Ryu, W.-H., Gittleson, F. S., Schwab, M., Goh, T. & Taylor, A. D. A mesoporous catalytic membrane architecture for lithium-oxygen battery systems. Nano Lett. 15, 434–441 (2015).

16. Schaltin, S., Vanhoutte, G., Wu, M., Bardé, F. & Fransaer, J. A QCM study of ORR-ORR and an in situ study of a redox mediator in DMSO for Li2O2 batteries. Phys. Chem. Chem. Phys. 17, 12575–12586 (2015).

17. Das, U., Lau, K. C., Redfern, P. C. & Curtiss, L. A. Structure and stability of lithium superoxide clusters and relevance to Li2O2 batteries. J. Phys. Chem. Lett. 5, 813–819 (2014).

18. Sangster, J. & Pelton, A. D. The Li-O (lithium-oxygen) system. J. Phase Equilibria 13, 296–299 (1992).

19. Lau, K. C., Curtiss, L. A. & G рейlee, J. Density functional investigation of the thermodynamic stability of lithium oxide bulk crystalline structures as a function of oxygen pressure. J. Phys. Chem. C 115, 23625–23633 (2011).

20. Kang, S., Mo, Y., Ong, S. P. & Ceder, G. A facile mechanism for recharging Li2O2 in Li2O2 batteries. Chem. Mater. 25, 3328–3336 (2013).

21. Hummers, W. S. & Offeman, R. E. Preparation of graphitic oxide. J. Am. Chem. Soc. 80, 1339 (1958).

22. Xu, Y., Sheng, K., Li, C. & Shi, G. Self-assembled graphene hydrogel via a one-step hydothermal process. ACS Nano 4, 4324–4330 (2010).

23. Zhuravlev, Y. N. & Obolonskaya, O. S. Structure, mechanical stability, and chemical bond in alkali metal oxides. J. Struct. Chem. 51, 1005–1013 (2010).

24. Kumar, S., Selvaraj, C., Munichandraiah, N. & Scanton, L. G. Gold nanoparticles anchored reduced graphene oxide as catalyst for oxygen electrode of rechargeable Li-O2 cells. RSC Adv. 3, 21706–21714 (2013).

25. Selvaraj, C., Kumar, S., Munichandraiah, N. & Scanton, L. G. Reduced graphene oxide-polypyrrole composite as a catalyst for oxygen electrode of high rate rechargeable Li2O2 cells. J. Electrochem. Soc. 161, A554–A560 (2014).

26. Oh, S.-H., Black, R., Pomerantseva, E., Lee, J.-H. & Nazar, L. F. Synthesis of a metallic mesoporous pyrochlore as a catalyst for lithium–O2 batteries. Nature Chem. 4, 1004–1010 (2012).

27. Ren, X., Zhang, S.-S., Tran, D. T. & Read, J. Oxygen reduction reaction catalyst on lithium-air battery discharge performance. J. Mater. Chem. 21, 4910–4915 (2011).

28. Mitchell, R. R., Gallant, B. M., Shao-Horn, Y. & Thompson, C. V. Mechanisms of morphological evolution of Li2O2 particles during electrochemical growth. J. Phys. Chem. Lett. 4, 1060–1064 (2013).

29. Ottakam Thotyil, M. M., Freunberger, S. A., Peng, Z. & Bruce, P. G. The carbon electrode in nonaqueous Li–O2 cells. J. Am. Chem. Soc. 135, 494–500 (2013).

30. Bikkarolla, S. K., Cumson, P., Joseph, P. & Papakonstantinou, P. Oxygen reduction reaction in electrochemically reduced graphene oxide. J. Mater. Chem. A 3, 1415–1428 (2015).

31. Antolini, E. Iridium as catalyst and cocatalyst for oxygen evolution/reduction in acidic polymer electrolyte membrane electrolyzers and fuel cells. ACS Catal. 4, 1426–1440 (2014).

32. Donkersloot, H. C. & Van Vucht, J. H. N. The crystal structure of IrLi, Ir3Li and LiRh3. J. Less Common Met. 50, 279–282 (1976).

33. Pouget, C. M. et al. The initial stages of template-controlled CaCO3 formation revealed by cryo-TEM. Science 325, 1455–1458 (2009).

Supplementary Information is available in the online version of the paper.

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Author Contributions J.L. and K.A. designed the experiments; Y.J.L., J.-B.P. and Y.S.J. synthesized the cathode materials; J.L., D.J.M. and J.W. performed and analysed the TEM imaging experiments; J.L., X.L., L.A.C. and Z.C. performed and analysed the X-ray measurements; J.L., X.L., Z.F.Z., D.Z. and H.-H.W. tested the cathode materials; M.A., A.S.-K. and B.K. performed the DEMS measurements, H.H.W., C.L. and S.B. performed Raman, XANES, XPS and FTIR experiments. K.C.L. and L.A.C. were responsible for the theoretical computations. L.A.C., K.A. and Y.-K.S. supervised the project; L.A.C., J.L. and K.A. wrote the paper. All of the authors discussed the results and reviewed the manuscript.

Author Information Atomic coordinates for the Li2O2 crystal structure from DFT can be obtained from the ICSD Database (http://www2.fiz-karlsruhe.de/icsd_home.html). Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to L.A.C. (curtiss@anl.gov) or K.A. (amine@anl.gov) or Y.-K.S. (yksun@hanyang.ac.kr).

Supplementary Information is available in the online version of the paper.
METHODS

Material preparation. Graphene oxide (GO) was prepared by a modified Hummers method21,22. Pristine reduced GO (rGO) was produced by reducing GO in polyol34. Specifically, a GO dispersion (1 mg ml~1~) in ethylene glycol (EG) was first prepared with the aid of sonication for 1 h. The solution pH was then adjusted to pH 13 with NaOH (2.5 M in EG). The reaction temperature was increased to 120 °C, and a reducing agent (NaBH₄) dissolved in EG was injected slowly. The solution was allowed to react for 1 h at this temperature and then cooled to room temperature. The precipitate was filtered, washed and dried under vacuum. The Ir–rGO composite was synthesized by a hydrothermal method. IrCl₃·3H₂O was added to 100 ml aqueous GO solution (0.67 mg ml~1~) with a weight ratio of 1Ir:1H₂O to GO of 1.9:1. The mixture was stirred for 2 h. The resulting solution was transferred to a Teflon-lined autoclave and then reacted hydrothermally at 180 °C for 12 h. The precipitate was filtered, washed and dried under vacuum. During hydrothermal treatment, Ir nanocrystals are obtained with simultaneous reduction of GO into rGO, without addition of strong base.

After synthesis, the Ir–rGO and rGO powders were dried at 80 °C under vacuum for 24 h. To prepare the oxygen electrode, the Ir–rGO and rGO were intimately mixed in an N-methyl-2-pyrrolidone (NMP) liquid and a polyvinylidene fluoride binder (PVDF) with a weight ratio of active ingredients to PVDF of 8:2. The slurry was coated onto a gas-diffusion layer (TGP-H-030 carbon paper, Toray) and dried for 12 h at 100 °C under vacuum to remove the residual solvent.

Electrochemical testing. Electrochemical testing was carried out using a Swagelok-type cell composed of a lithium metal anode, electrolyte (1 M LiClO₄/THF), and a lithium foil current collector. The half-cells were assembled in an argon-filled glovebox. Aliquots of the samples were then integrated into conventional 1D patterns (intensity versus 2θ) from the air. The HE-XRD patterns were collected in the transmission mode.

During the course of the measurements, a high-energy X-ray beam hit the sample from the air. The HE-XRD patterns were collected in the transmission mode. For the simulation of the solvent, a smaller ether solvent molecule, that is, dimethoxyethane (DME) was used instead of tetraethylene glycol dimethyl ether (TEGDME) in order to reduce the computational cost. To investigate the thermodynamic and dynamic stability of the system at room temperature, all the structures from the DFT optimizations were then thermally equilibrated at T = 300 K using AIMD simulations based on an Nose-Hoover NVT-ensemble with a time step of 1 fs.

For the ab initio prediction of Electron Paramagnetic Resonance (EPR) g-tensors of the crystalline solids LiO₂ and NaO₂, we have used the DFT plane wave code Quantum Espresso simulation package49 in which the Gauge-Including Projector Augmented Plane Wave (GIPAW) approach50 has been implemented. To be consistent with our VASP calculations, we employed the PBE functional and Martins-Troullier norm-conserving pseudopotentials generated by D Ceresoli (https://sites.google.com/site/dceresoli/pseudopotentials). Throughout the simulation, a plane wave energy cutoff of 20 Ry was used. The PAW method38 was used for all the calculations. To calculate the g-tensors, we used the PBE functional and Martins-Troullier norm-conserving pseudopotentials. For the simulation of the LiO₂ surface with some solvent molecules on it, the Van der Waals method of 

Sample size. No statistical methods were used to predetermine sample size.

34. Ha, H.-W., Kim, I. Y., Hwang, S.-J. & Ruoff, R. S. One-pot synthesis of platinum nanoparticles embedded on reduced graphene oxide for oxygen reduction in methanol fuel cells. Electrochem. Solid-State Lett. 14, S70–S73 (2011).
35. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 6, 15–50 (1996).
36. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758–1775 (1999).
37. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).
38. Blöchl, P. E. Projector augmented-wave method. Phys. Rev. B 50, 17953–17979 (1994).
39. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. J. Comput. Chem. 27, 1787–1799 (2006).
40. Giannozzi, P. et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. J. Phys. Condens. Matter 21, 395502 (2009).
41. Pickard, C. J. & Mauri, F. First-principles theory of the EPR g tensor in solids: defects in quartz. Phys. Rev. Lett. 88, 086403 (2002).
42. Ziegler, M., Rosenfeld, M., Kaenzig, W. & Fischer, P. Strukturuntersuchungen an Alkalihyperoxiden. Helvetica Physica Acta 49, 57–90 (1976).
43. Adrian, F. J., Cochran, E. L. & Bowers, V. A. ESR spectra and structures of Na₂O and NaO₂. J. Chem. Phys. 59, 56–60 (1973).
44. Lindsay, D. M. & Garland, D. A. ESR spectra of matrix-isolated lithium superoxide. J. Phys. Chem. 91, 6158–6161 (1987).