Potassium Salts as Electrolyte Additives in Lithium-Oxygen Batteries

Imanol Landa-Medrano,^{1,2} Mara Olivares-Marín,^{2,3} Benjamin Bergner,^{4,5} Ricardo Pinedo,⁴ Andrea Sorrentino,⁶ Eva Pereiro,⁶ Idoia Ruiz de Larramendi,¹ Jürgen Janek,⁴ Teófilo Rojo^{1,7} and Dino Tonti^{2}*

¹ Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU) Barrio Sarriena s/n, 48940 Leioa - Bizkaia, Spain

² Institut de Ciència de Materials de Barcelona, Consejo Superior de Investigaciones Científicas (ICMAB-CSIC), Campus UAB Bellaterra, Barcelona, Spain

³ Present adress: Centro Universitario de Mérida, Universidad de Extremadura, Avda. Santa Teresa de Jornet 38, Mérida, Spain

⁴ Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 58, 35392 Gießen, Germany

⁵ Present address: Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK

⁶ ALBA Synchrotron Light Source, MISTRAL Beamline – Experiments Division, 08290 Cerdanyola del Vallès, Barcelona, Spain

⁷ CIC EnergiGUNE, Albert Einstein 48, 0150, Miñano, Spain

AUTHOR INFORMATION

Corresponding Author

*E-mail: dino.t@csic.es.

Abstract

The stabilization of the intermediates formed during oxygen reduction reaction and their efficient solubilization and diffusion is a crucial issue that needs to be improved in non-aqueous lithium oxygen batteries. By adding 0.1 M K^+ (as KOTf salt) to the electrolyte we have observed remarkable improvements in the rate capability of the discharge process. The K^+ cation facilitates a more homogeneous discharge product deposition in the porous cathode. Instead, as evidenced by synchrotron measurements, we find that K^+ does not influence the cell chemistry, suggesting that it rather assists the superoxide solvation, thus enhancing the solution-based growth of the discharge products. In addition, if iodide (I^-) is added as redox mediator we find an extended cycle life when K^+ instead of Li^+ is used as cation. This finding remarks the benefits of stabilizing the oxygen reduction products in the electrolyte leading to a solution-based mechanism.

Introduction

Non-aqueous alkali-oxygen batteries are subject of strong interest due to their high theoretical gravimetric energy density, particularly lithium-oxygen batteries (LOBs) with practical devices expected to reach 500-900 Wh kg⁻¹, three times higher than that of commercial lithium-ion batteries.^{1,2} Unfortunately these values are still far from reality due to design,^{3,4} side reactions^{5,6} and low efficiency issues.⁷ Most investigations have been focusing on the cathode and the oxygen reduction reaction (ORR), where the main steps can be described by equations 1-3:^{8,9}

The first discharge product formed is lithium superoxide dissolved in the electrolyte (reaction 1), which later evolves to lithium peroxide, being much more stable in the battery environment, either chemically (reaction 2), or electrochemically (reaction 3). By stabilizing the superoxide intermediate in solution, and/or increasing its concentration, it may be possible to control the morphology of the deposited Li₂O₂. In effect, transitions from film-like to particle-shaped Li₂O₂ discharge products have been obtained by several means: decreasing the discharge current density,¹⁰⁻¹³ stirring the electrolyte,¹⁴ using electrolytes with higher Gutmann donor number (DN),¹⁵ or by controlling the concentration of residual water.^{16,17}

Abraham *et al.* observed that both the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) were favored when Li⁺ was substituted by larger monovalent cations, and explained this effect based on Pearson's hard and soft acid and base (HSAB) theory:¹⁸ Larger

cations are softer Lewis acids that coordinate more strongly with the soft base O_2^- . Considering that the superoxide radical can react with both electrolyte¹⁹ and carbon electrode^{20,21}, a complexed state would also help to prevent the degradation of the cell components. Interestingly, Sharon *et al.* evidenced by the use of different anions in the electrolyte that the reduced dissociation of the electrolyte salt delays the interaction between Li^+ and LiO_2 leading to an enhanced solution phase mechanism.¹³

The insulating nature of the precipitated peroxide product (reactions 2 and 3) usually results in high charge overpotentials that can lead to the oxidation of the carbon electrode and the electrolyte.^{5,22} Redox mediators (RM) have been proposed to improve rechargeability. These compounds, which are dissolved in the electrolyte, can be oxidized (RM^+) at low overpotentials during charge, diffuse to the surface of non-conductive Li_2O_2 crystals, oxidizing them and returning to their initial state (RM).²³ The activity of several molecules has already been studied, such as tetrathiafulvalene (TTF),²⁴ iron phthalocyanine (FePc),²⁵ 2,2,6,6-tetramethylpiperidinyloxy (TEMPO)^{26,27} and iodide (I^-).^{23,28-29} Molecules with redox potential below 3 V vs. Li^+/Li such as ethyl viologen (EtV^{2+}),³⁰ quinones³¹ and organic radicals³² can instead mediate discharge, allowing faster rates and a better control of the peroxide precipitation.

In this work, we used potassium trifluoromethanesulfonate (KOTf, potassium triflate) as an additive and K^+ source to the lithium electrolyte, observing a beneficial effect on the electrochemical performance of a LOB. Potassium-oxygen batteries have been successfully cycled based on the formation and decomposition of potassium superoxide (KO_2)³³ and potassium impurities in the carbonaceous material used in oxygen electrode have been demonstrated to improve the performance of Li- O_2 batteries.³⁴ However, as far as we know, potassium has not been used as additive in the electrolyte so far. We found that K^+ improves the

ORR rate capability and leads to more homogeneous deposits without altering its chemistry. Additionally, we observed a synergy of K^+ coupled to the I^- redox mediator, extending the LOB cycle life beyond the use of I^- alone. This result is consistent with the recent report of Lee *et al.* on a substantially improved cycle life by using CsI as additive.³⁵ However, while the authors attributed the effect to Cs^+ suppressing dendrite formation at the anode through a self-healing electrostatic shield mechanism,³⁶ we find evidence of improved reversibility at the cathode side. Whatever the actual mechanism, KI can also be considered an interesting additive for the improvement of the battery performance.

Experimental Methods

Cathode fabrication

Carbon cathodes were prepared by grinding in a mortar carbon black (Super P, M. M. M. Carbon) and polyvinylidene fluoride (PVdF) in a weight ratio of 9:1 and adding N-methylpyrrolidone (NMP). The slurry obtained was used to impregnate a stainless steel mesh (AISI 416, 180 meshes per inch, Advent Research Materials Ltd.) and finally dried at 100 °C for 12 h. The electrode loading was of the order of 1 mg cm⁻². In addition, carbon-coated Au TEM grids (200 mesh, 3.05 mm diameter, 16 µm metal thickness, CF200-Au from EMS) were also used directly as a cathode for synchrotron characterization. TEM grids used as oxygen electrodes were coated following the same procedure. Total carbon mass in the electrode was around 0.03 mg.

Electrochemical studies.

The electrolyte consisted of dried (100 °C under vacuum) 1 M lithium trifluoromethanesulfonate (LiOTf, 99.995% trace metal bases, Sigma-Aldrich) dissolved in tetraethylene glycol dimethyl ether (TEGDME,

$\geq 99\%$, Sigma-Aldrich). In order to analyze the effect of K^+ addition to the containing LiOTf electrolyte a 0.1 M potassium trifluoromethane sulfonate (KOTf, 98%, Sigma-Aldrich) and 1 M LiOTf TEGDME-based electrolyte was prepared. For redox mediated measurements 100 mM of potassium iodine (KI, Sigma-Aldrich) were added to the electrolyte. Lithium iodine (LiI, Sigma-Aldrich) containing electrolyte was also prepared for comparison with KI. Electrolytes were prepared inside an Ar-filled glovebox and stirred overnight in presence of 4 Å molecular sieves (Sigma-Aldrich). The final water content was below 30 ppm as measured by Karl-Fisher titration (Metrohm).

A two-electrode Swagelok-type cell similar to the one described by Bender *et al.*³⁷ was used for galvanostatic and cyclic voltammetry (CV) measurements.³⁸ It consisted of a Li metal foil anode, a glass fiber filter (filterLab MFV1, 260 μm thick) separator soaked with $\sim 100\ \mu\text{L}$ electrolyte and the previously described cathode. Cell assembly was carried out inside an Ar-filled glovebox.

For the electrochemical measurements, the argon was replaced by oxygen inside the cell. A constant flux of oxygen was passed through the oxygen inlet system for 30 minutes in order to eliminate any moisture traces from the pipes. After that, Ar of the cell was purged by O_2 during 30 seconds, after which the cell was closed. Electrochemical measurements were carried out using a Biologic VMP3 multichannel potentiostat.

All pressure data were recorded using a PAA-33X absolute pressure sensor, a K104B USB computer adapter, and the software Read30 v2.10 (all from Omega Engineering). The volumes of the different gas reservoirs were determined by parallel use of the pressure sensor and a calibrated syringe (Hamilton). The oxygen consumption and the gas evolution were calculated from the recorded pressure data on the basis of the ideal gas law.

Product characterization

Closed cells were transferred to the Ar-filled glovebox where they were disassembled avoiding the contact of the discharge products with ambient air. The oxygen electrodes were washed with 1,2-dimethoxyethane prior to their analysis in order to remove the electrolyte traces.

Discharge and charge product characterization was carried out by X-ray powder diffraction (XRD) on an X'pert pro (PANalytical) diffractometer using the Cu K α radiation ($\lambda = 1.5418\text{\AA}$). XRD patterns were recorded between 30° and 60° 2θ with a step size of 0.02° . A self-made gas-tight sample holder was used for these structural characterizations.

Discharge products in presence and absence of KOTf were characterized using energy-resolved full-field transmission soft X-ray microscopy (TXM) performed at the MISTRAL beamline of the ALBA synchrotron.^{39,40} Carbon-coated Au TEM grids after electrochemical test were stored in Ar-filled glove box and washed with DME and hexane to remove the electrolyte before characterization. XANES images (2 s exposure time, effective pixel size 10 nm, field of view $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$) were collected from 525 eV to 550 eV in 120 steps, varying the energy across the O K-edge with a spectral sampling of 0.25 eV. The objective zone plate lens and the CCD detector positions were automatically adjusted to maintain focus and constant magnification. In this way, 2D maps of the oxygen chemical state of the principal possible reaction products involved were obtained with a full XANES spectrum at each pixel. The total acquisition time necessary to acquire a full XANES TXM spectrum was about 2 hours, including the flat field acquisition at each energy step. The images of the energy stack were automatically aligned respect with the first one, shifting each image the number of pixels which maximize the normalized cross-correlation between the central region of each image (300×500 pixels, $H \times V$) and the central region of the first one.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI5000 Versa Probe spectrometer using a monochromatic Al K α radiation ($h\nu = 1486.6\text{ eV}$). The peaks were recorded with constant pass energy of 23.5 eV. The diameter of the irradiated area was $\sim 200\text{ }\mu\text{m}$. To minimize charging effects a dual beam charge neutralization system was used.

Photoelectron spectra were fitted with a Casa XPS software with Shirley backgrounds and 100% Gaussian curves. All spectra were charge corrected to a binding energy from hydrocarbons contamination on top of the surface using the C 1s peak at 284.8 eV. Electrodes were transferred from the glovebox using an air-tight sample holder.

Results and Discussion

The effect of adding K^+ to the electrolyte was studied comparing the electrochemical performance of two LOBs with different electrolytes; one of them consisted of K^+ free, 1 M LiOTf in TEGDME while the second one was 0.1 M KOTf and 1 M LiOTf in TEGDME (Figure 1).

Figure 1. Electrochemical performance of lithium-oxygen batteries with (orange line) and without (green) 0.1 M KOTf in the electrolyte. (a) Cyclic voltammetry at a scan rate of 20 mV s⁻¹. (b) First galvanostatic discharge profiles at 0.1 mA cm⁻². (c) First galvanostatic discharge profile at 1.5 mA cm⁻². (d) Galvanostatic cycling of a battery with an electrolyte containing 0.1 M KOTf in a voltage range of 2 and 4.2 V at 0.1 mA cm⁻².

The CV measurement, shown in Figure 1.a, evidences that the potentials of electrochemical processes (onsets at 2.6 V for the cathodic scan and 3.1 and 3.6 V for the anodic scan) were unaffected by the presence of K⁺ in the electrolyte. However, both cathodic and anodic currents are enhanced by a factor of almost two. This was also observed by Abraham *et al.* when they used salts of different monovalent cations at a concentration of 0.025 M.⁸ In that work, however,

the onset potentials during anodic scans were increasing with smaller cations. Instead, the anodic scan in Fig. 1.a reveals the same onset potential for the two observed processes after adding K^+ . It is widely accepted that the first process in the anodic scan starting at 3.1 V corresponds to LiO_2 oxidation, while the second process at 3.6 V is related to Li_2O_2 oxidation.⁴¹ In addition, the observed anodic current is only slightly higher in presence of K^+ revealing that it does not influence the OER chemistry.

Galvanostatic discharges of LOBs with and without K^+ ions in the electrolyte were carried out at 0.1 mA cm^{-2} (Figure 1.b) and 1.5 mA cm^{-2} (Figure 1.c). At 0.1 mA cm^{-2} almost no differences were observed in the discharge profile or the capacity of the battery. Instead, at the higher current density of 1.5 mA cm^{-2} the electrolyte with K^+ showed both lower overpotential and higher discharge capacity. Galvanostatic discharges in Figure 1.c are similar to those reported using a ORR redox mediator.^{30,32} In those cases, the higher rate capability was attributed to the electron transfer from the electrode to the mediator, which then promotes a solution-mediated ORR, that finally leads to higher discharge capacity. In the present case, no mediator was added, but a similar effect is achieved by the addition of K^+ that favors a solution-mediated mechanism. Adams and coworkers suggested that kinetics, electrolyte and surface interactions have significant impact on the reaction route, superoxide stabilization has major implications for ORR, via solvation and competition to the 2nd electron reduction to form solid peroxide.¹⁰ In effect, they showed that at low current densities, the ORR is solution-mediated leading to large toroidal particles.¹⁰ This morphology can also be favored by solvating additives, including water.^{16,17} In this regime the current density is low enough compared to the rate of LiO_2 desorption and diffusion in the electrolyte, which is necessary for solution-phase mediation.¹⁰ Since this additional mass transport step is not rate-limiting, the presence of K^+ has little effect,

so that we observe similar electrochemical profiles and toroid formation. In contrast, at higher current densities LiO_2 desorption becomes rate limiting, hindering the solution phase mechanism so that surface-mediated ORR takes over, with lower discharge voltage and capacity. As explained by Abraham, K^+ contributes to stabilize the superoxide anion in the bulk of the electrolyte due to the favorable soft acid-base interaction.⁸ This stronger interaction, possibly through KO_2 formation, likely favors superoxide desorption and its mass transfer from the electrode, allowing solution-phase mediation. As a consequence, in presence of K^+ at high current discharge capacity and the discharge voltage plateau are increased, which implies an improved rate capability. This mechanism originated by the superoxide interaction with cation is the likely cause of the increasing cathodic current in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ as reported by Abraham⁸.

The rechargeability remains equally poor, as shown by a galvanostatic cycling at 0.1 mA cm^{-2} in a voltage range of 2-4.2 V, leading to fast capacity fading (Figure 1.d). It has to be noted that by the addition of K^+ to the electrolyte one could expect the formation of KO_2 , similarly to K- O_2 cells.³³ Experimental oxidation of KO_2 during charge, however, occurs at $\sim 2.8 \text{ V}$ vs. Li^+/Li (2.62 V vs. K^+/K in the work by Ren *et al.*)³³ and, therefore, the lack of a plateau at such potential evidences the absence of KO_2 . This behavior proves that K^+ does not influence the OER, which is in good agreement with the CV data in Figure 1.a. Consequently, an additional agent is required in order to improve the OER and the cycling performance of the cell.

As mentioned in the introduction, CsI addition to the electrolyte has been reported to remarkably improve the rechargeability of the Li- O_2 battery combining the effect of the I^- redox mediator with suppression of Li dendrites at the anode by Cs^+ .³⁵ This is attributed to a self-healing electrostatic shield mechanism that requires a cation with reduction potential lower than Li^+ .³⁶

According to the Nernst equation this condition can be attained even with a cation of higher standard reduction potential if present at low concentration. In effect, the K^+ standard potential is just 0.1 V higher than the one for Cs^+ ⁴² and could present a similar behavior. To prove if K^+ also had an effect on charging we tested its combined effect with I^- , comparing cells with and without the addition of 0.1 M LiI or KI to the 1 M LiOTf in TEGDME electrolyte (Figure 2).

Figure 2. Galvanostatic cycles of LOBs between 2 and 4.2 V at 0.1 mA cm⁻² with a cutoff capacity of 500 mA h g⁻¹. (a) Profiles without additives, (b) with 0.1 M LiI redox mediator and (c) with 0.1 M KI redox mediator in the electrolyte. (d) Comparison of the discharge (line-connected dots) and charge (circles) capacities obtained with 0.1 M LiI and with 0.1 M KI.

These cells were cycled at a current density of 0.1 mA cm⁻² limiting the discharge and charge capacity to 500 mA h g⁻¹. Even when the discharge capacity is limited, below 4.2 V the cell

without redox mediator could only oxidize a small part of the discharge products deposited in the cathode, leading to a fast decay of the discharge capacity after few cycles (Figure 2.a). Thus, the cell could only reach 60% of the cutoff capacity (500 mAh g^{-1}) already after 5 galvanostatic cycles. As expected, when LiI was used, the charge reaction was enhanced, with a clear plateau below 4 V, leading to an improved capacity retention, with over 60% of the capacity for at least 20 cycles (Figure 2.b). This capacity, however, decreased rather fast in the following cycles. With 0.1 M KI (Figure 2.c) a stable first discharge plateau is observed at 2.55 V similar to the previous cases. The process occurring at 3.0 V, which was previously observed in the cell with LiI during charge, was also detected with an apparently similar evolution during the first 10 cycles. However, beyond this point discharge capacity was retained between 350 and 450 mA h g^{-1} when KI was used while the capacity fade was much faster in presence of LiI. Consequently, we detect a synergetic effect of K^+ and I^- clearly improving the cycling performance of the LOB. At closer inspection, we observe consistently lower potentials of the charge plateaus in presence of K^+ . As shown in Figure S1, I^- oxidation contributes to capacity with the initial 3.2-3.4 V charging plateau. In fact, a plateau with similar capacity appears from the second discharge, indicating reduction of the produced I_3^- . Similar to the rest of the profile, also this part suffers a progressive shortening, but in presence of K^+ this decay is slower as well. The following plateau at 3.5-3.8 V can be attributed to I_3^- -mediated OER, while the final increasing part rather corresponds to partial carbonate removal. As shown in Figure S2 the extension of this removal, by changing the voltage and capacity limits, clearly affects the cycle life. The lower charging overpotentials and persistently longer OER plateaus with KI suggest that K^+ interferes with formation of ORR products making their removal more quantitative. This improvement is already observed in the first 5 cycles, while discharge curves equally retain the initial potential

with and without potassium. Thus, at this stage the possible effect of dendrite formation over the anode still can be considered not relevant, as it would introduce a thicker passivation layer, equally increasing the overpotential for the following discharge. Therefore, although a benefit also on the lithium interface cannot be ruled out, we believe that K^+ cooperates to a more reversible process at the cathode.

XPS analysis of the lithium anode reveals the presence of both I^- and K^+ at the surface (Figure 3). While K exhibits just one signal (highlighted in orange), three different signals can be observed for the case of iodine. It must be noted that the identification of the chemical nature of potassium from XPS is challenging. In contrast, the iodine spectrum evidences not only that I^- is the main species, but also that secondary products such as I_2 or IO_4^- can be deposited or chemisorbed at the anode surface. Iodide species could be expected from the precipitation of the additive, its reaction with the anode or the reduction of the I_2 migrated from the cathode towards the anode during the charge process. This I_2 shuttling was suggested in our previous work⁴³ and the present results confirm this process. Finally, the presence of oxidized species can be related with further parasitic reactions. The deposition of iodine species explains the progressive shortening of the 3.2-3.4 V charging plateau. Instead, the presence of potassium discards a possibility that has been reported in literature by adding In^{3+} .⁴⁴ K^+ in the electrolyte does not suppress the reaction of I^- with the Li electrode. Moreover, the deposition of K^+ on the anode points out the need of limiting its migration and deposition on this electrode; for this purpose the introduction of selective membranes is considered a promising approach.²⁷

Figure 3. XPS measurements on the anode after 1 cycle (2-4.2 V) using a KI additive in the electrolyte: C 1s and K2p (a) and I 3d regions (b).

XRD measurements of the oxygen electrode (Figure S3) confirmed Li_2O_2 formation (reflections at 32.9° and 34.9° , JDCPS 74-0115) during discharge and its removal after recharge to 3.8 V with the KI additive. One could expect the deposition of KO_2 (JDCPS 77-0211) in the electrode due

to the addition of K^+ to the electrolyte. XRD pattern, however, did not evidence the presence of such specie as no signal was detected at $2\theta = 31.37^\circ$. LiOH formation was also not detected, contrarily to the report by Liu *et al.* where LiOH has been identified as the main discharge product in a water containing Li-O₂ battery with LiI as RM.²⁹ The difference could be attributed to our lower water content.

We have previously obtained chemically correlated images of Li/O₂ discharge products by transmission soft X-ray microscopy (TXM),⁴⁵ and the same method has been applied here to inspect whether the use of K^+ affected the distribution and composition of the deposits after the discharge of the cell to 2.0 V in presence and absence of 0.1 M K^+ . Analyses of the O K-edge XANES spectra of the TEM grids (Figure 4.a) reveal the presence of LiO₂, Li₂O₂ and Li₂CO₃ with very similar proportions for both electrolyte compositions. From the absence of superoxide and carbonate reflections in the XRD of the oxygen electrode we infer an essentially amorphous character for these components. TXM images revealed toroidal particles in both cases, but their size distribution was significantly different (Figure 4.b): the presence of K^+ led to a more homogeneous particle size. Instead, no significant chemical differences in the discharge products were observed, given the similar XANES spectra.

Figure 4. (a) O K-edge XANES spectra of the reference materials (Li_2O_2 and Li_2CO_3) and the discharge particles obtained at the carbon coated Au TEM grid after being fully discharged at 100 mA per total gram of carbon in a Li–O₂ cell in presence and absence of KOTf. (b) TXM images of the discharge products obtained in presence and absence of KOTf. Increase of the $\text{LiO}_2/\text{Li}_2\text{O}_2$ ratio and the Li_2CO_3 fraction are represented by increasing the color heat at each pixel.

The essentially similar chemistry of the discharge and charge processes has been confirmed also quantitatively by monitoring the cell pressure during the galvanostatic experiments. These measurements allow quantifying the number of gas molecules consumed or released per electron exchanged at the electrode. Figure 5 shows the voltage and pressure profiles of the cells without RM and with 0.1 M LiI and 0.1 M in the electrolyte.

Figure 5. First galvanostatic cycle of the Li-O₂ cell (a) without redox mediator, (b) adding 0.1 M LiI and (c) adding 0.1 M KI to the electrolyte. Relative pressure variations are represented in grey for each galvanostatic cycle.

During discharge all values are close to the ideal $2 N(e^-)/N(\text{gm})$ (i.e., 2 electrons per gas molecule) for the reduction of O_2 to Li_2O_2 , confirming that the electrochemically generated discharge products were chemically identical. After charge to 4.2 V not all the O_2 consumed during discharge was recovered, leading to ratios of $N(e^-)/N(\text{gm})$ close to 3. This can be attributed to parasitic reactions following the ideal ORR process. Lower values were found with iodide mediator, confirming its role for a higher reversibility and efficient charge of the battery. Again, we can infer that differences using K^+ instead of Li^+ in the electrochemically generated products were negligible.

From these results we deduce that K^+ does not affect the cell chemistry or interfere in the reaction path, but enhances the kinetics of the precipitation process. Due to the high soft acid-base affinity with superoxide, K^+ promotes a higher rate capability displacing the reduction of dioxygen toward its superoxide product, and thus leading to a higher superoxide concentration in solution. This high concentration could lead to a better nucleation and more homogeneous particle growth as suggested by images of the precipitate. The more distributed peroxide precipitation, results in a slower passivation and an easier oxidation. In effect, previous reports have demonstrated a significant dependence of the charge potential on the size of the discharged particles.^{10,46} The more homogeneous precipitate leads to lower overpotentials and thus larger cycle life is observed.

Conclusions

Two positive effects of K^+ addition to the electrolyte of LOBs have been observed: 1) an improved discharge rate capability; 2) sustained cycling in presence of an oxidation redox

mediator such as iodide. We found that K^+ does not affect the cell chemistry, but favors a more homogeneous discharge particle growth, which could be related to the stabilization of superoxide in the electrolyte by interaction with K^+ . The easier and more distributed precipitation allows supporting higher discharge currents. This more homogeneous precipitate facilitates the attack by oxidized mediators during charge, which reduces overpotentials and the associated irreversible side reactions, therefore improving capacity retention. This synergetic improvement of the cycling performance makes KI a better choice than LiI as additive for LOBs. Indeed, an electrolyte additive as K^+ is one of the simplest, safest, and most stable additives that can be conceived, and encourages research on alternative mechanisms of controlling the Li_2O_2 discharge process for increased cell reversibility.

Supporting Information Description.

XRD analysis of discharge products and additional electrochemical studies in presence and absence of additives.

Acknowledgment

This work has been partially financed by the Spanish Ministry of Economy, Industry and Competitiveness, through the “Severo Ochoa” Programme for Centres of Excellence in R&D (SEV- 2015-0496), through projects MAT2013-41128-R, MAT2016-78266-P, MAT2015-68394-R, by the “Fondo Europeo de Desarrollo Regional” (FEDER), by the Eusko Jaurlaritza/Gobierno Vasco (through project IT-570-13), and by the Generalitat de Catalunya (grant 2014 SGR 1505). I. Landa-Medrano thanks the Universidad del País Vasco (UPV/EHU)

for his predoctoral fellowship. M. Olivares-Marín acknowledges CSIC for a JAE-DOC research contract co-funded by the European Social Fund. J. Janek acknowledges financial support by BMBF (Federal Ministry of Education and Research) within the project BENCHBATT. The x-ray microscopy experiments were performed at MISTRAL beamline at ALBA Synchrotron with the collaboration of ALBA staff.

References

- (1) Lu, J.; Li, L.; Park, J.; Sun, Y.; Wu, F.; Amine, K. Aprotic and Aqueous Li–O₂ Batteries. *Chem. Rev.* **2014**, *114*, 5611–5640.
- (2) Lu, Y.-C.; Gallant, B. M.; Kwabi, D. G.; Harding, J. R.; Mitchell, R. R.; Whittingham, M. S.; Shao-Horn, Y. Lithium–Oxygen Batteries: Bridging Mechanistic Understanding and Battery Performance. *Energy Environ. Sci.* **2013**, *6*, 750–768.
- (3) Albertus, P.; Girishkumar, G.; McCloskey, B.; Sánchez-Carrera, R. S.; Kozinsky, B.; Christensen, J.; Luntz, A. C. Identifying Capacity Limitations in the Li/Oxygen Battery Using Experiments and Modeling. *J. Electrochem. Soc.* **2011**, *158*, A343–A351.
- (4) Gallagher, K. G.; Goebel, S.; Greszler, T.; Mathias, M.; Oelerich, W.; Eroglu, D.; Srinivasan, V. Quantifying the Promise of Lithium–Air Batteries for Electric Vehicles. *Energy Environ. Sci.* **2014**, *7*, 1555–1563.
- (5) McCloskey, B. D.; Scheffler, R.; Speidel, A.; Girishkumar, G.; Luntz, A. C. On the Mechanism of Nonaqueous Li – O₂ Electrochemistry on C and Its Kinetic Overpotentials. *J. Phys. Chem. C* **2012**, *116*, 23897–23905.
- (6) McCloskey, B. D.; Speidel, A.; Scheffler, R.; Miller, D. C.; Viswanathan, V.; Hummelshøj, J. S.; Nørskov, J. K.; Luntz, A. C. Twin Problems of Interfacial Carbonate

- Formation in Nonaqueous Li-O₂ Batteries. *J. Phys. Chem. Lett.* **2012**, *3*, 997–1001.
- (7) McCloskey, B. D.; Garcia, J. M.; Luntz, A. C. Chemical and Electrochemical Differences in Nonaqueous Li-O₂ and Na-O₂ Batteries. *J. Phys. Chem. Lett.* **2014**, *5*, 1230–1235.
 - (8) Abraham, K. M. Electrolyte-Directed Reactions of the Oxygen Electrode in Lithium-Air Batteries. *J. Electrochem. Soc.* **2014**, *162*, A3021–A3031.
 - (9) Laoire, C. O.; Mukerjee, S.; Abraham, K. M.; Plichta, E. J.; Hendrickson, M. A. Influence of Nonaqueous Solvents on the Electrochemistry of Oxygen in the Rechargeable Lithium–Air Battery. *J. Phys. Chem. C* **2010**, *114*, 9178–9186.
 - (10) Adams, B. D.; Radtke, C.; Black, R.; Trudeau, M. L.; Zaghbi, K.; Nazar, L. F. Current Density Dependence of Peroxide Formation in the Li-O₂ Battery and its Effect on Charge. *Energy Environ. Sci.* **2013**, *6*, 1772–1778.
 - (11) Read, J. Characterization of the Lithium/Oxygen Organic Electrolyte Battery. *J. Electrochem. Soc.* **2002**, *149*, A1190–A1195.
 - (12) Horstmann, B.; Gallant, B.; Mitchell, R.; Bessler, W. G.; Shao-Horn, Y.; Bazant, M. Z. Rate-Dependent Morphology of Li₂O₂ Growth in Li-O₂ Batteries. *J. Phys. Chem. Lett.* **2013**, *4*, 4217–4222.
 - (13) Mitchell, R. R.; Gallant, B. M.; Shao-Horn, Y.; Thompson, C. V. Mechanism of the Morphological Evolution of Li₂O₂ Particles During Electrochemical Growth. *J. Phys. Chem. Lett.* **2013**, *4*, 1060–1064.
 - (14) Aklalouch, M.; Olivares-Marín, M.; Lee, R. C.; Palomino, P.; Enciso, E.; Tonti, D. Mass-transport Control on the Discharge Mechanism in Li-O₂ Batteries Using Carbon Cathodes with Varied Porosity. *ChemSusChem* **2015**, *8*, 3465–3471.
 - (15) Johnson, L.; Li, C.; Liu, Z.; Chen, Y.; Freunberger, S. A.; Tarascon, J.-M.; Ashok, P. C.; Praveen, B. B.; Dholakia, K.; Bruce, P. G. The Role of LiO₂ Solubility in O₂ Reduction in Aprotic Solvents and its Consequences for Li-O₂ Batteries. *Nat. Chem.* **2014**, *6*, 1091–1099.

- (16) Schwenke, K. U.; Metzger, M.; Restle, T.; Piana, M.; Gasteiger, H. A. The Influence of Water and Protons on Li_2O_2 Crystal Growth in Aprotic Li- O_2 Cells. *J. Electrochem. Soc.* **2015**, *162*, A573–A584.
- (17) Aetukuri, N. B.; McCloskey, B. D.; García, J. M.; Krupp, L. E.; Viswanathan, V.; Luntz, A. C. Solvating Additives Drive Solution-Mediated Electrochemistry and Enhance Toroid Growth in Non-Aqueous Li- O_2 Batteries. *Nat. Chem.* **2014**, *7*, 50–56.
- (18) Pearson, R. G. Hard and Soft Acids and Bases. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.
- (19) Freunberger, S. A.; Chen, Y.; Peng, Z.; Griffin, J. M.; Hardwick, L. J.; Bardé, F.; Novák, P.; Bruce, P. G. Reactions in the Rechargeable Lithium- O_2 Battery with Alkyl Carbonate Electrolytes. *J. Am. Chem. Soc.* **2011**, *133*, 8040–8047.
- (20) Itkis, D. M.; Semenenko, D. A.; Kataev, E. Y.; Belova, A. I.; Neudachina, V. S.; Sirotina, A. P.; Hävecker, M.; Teschner, D.; Knop-Gericke, A.; Dudin, P.; et al. Reactivity of Carbon in Lithium-Oxygen Battery Positive Electrodes. *Nano Lett.* **2013**, *13*, 4697–4701.
- (21) Landa-Medrano, I.; Pinedo, R.; Ortiz-Vitoriano, N.; Ruiz de Larramendi, I.; Rojo, T. A Step Forward in the Development of Stable Lithium-Oxygen Batteries. *ChemSusChem* **2015**, *8*, 3932–3940.
- (22) Thotiyl, M. M. O.; Freunberger, S. A.; Peng, Z.; Bruce, P. G. The Carbon Electrode in Nonaqueous Li- O_2 Cells. *J. Am. Chem. Soc.* **2013**, *135*, 494–500.
- (23) Lim, H. D.; Song, H.; Kim, J.; Gwon, H.; Bae, Y.; Park, K. Y.; Hong, J.; Kim, H.; Kim, T.; Kim, Y. H.; et al. Superior Rechargeability and Efficiency of Lithium-Oxygen Batteries: Hierarchical Air Electrode Architecture Combined with a Soluble Catalyst. *Angew. Chemie* **2014**, *126*, 4007–4012.
- (24) Chen, Y.; Freunberger, S. A.; Peng, Z.; Fontaine, O.; Bruce, P. G. Charging a Li- O_2 Battery Using a Redox Mediator. *Nat. Chem.* **2013**, *5*, 489–494.
- (25) Sun, D.; Shen, Y.; Zhang, W.; Yu, L.; Yi, Z.; Yin, W.; Wang, D.; Huang, Y.; Wang, J.; Wang, D.; et al. A Solution-Phase Bifunctional Catalyst for Lithium-Oxygen Batteries. *J.*

- Am. Chem. Soc.* **2014**, *136*, 8941–8946.
- (26) Bergner, B. J.; Schürmann, A.; Peppler, K.; Garsuch, A.; Janek, J. TEMPO: A Mobile Catalyst for Rechargeable Li-O₂ Batteries. *J. Am. Chem. Soc.* **2014**, *136*, 15054–15064.
 - (27) Bergner, B. J.; Busche, M. R.; Pinedo, R.; Berkes, B. B.; Schröder, D.; Janek, J. How to Improve Capacity and Cycling Stability for Next Generation Li-O₂ Batteries: Novel Approach with a Solid Electrolyte and Elevated Redox Mediator Concentrations. *ACS Appl. Mater. Interfaces* **2016**, *8*, 7756–7765.
 - (28) Kim, D. S.; Park, Y. J. Effect of Multi-Catalysts on Rechargeable Li – Air Batteries. *J. Alloys Compd.* **2014**, *591*, 164–169.
 - (29) Liu, T.; Leskes, M.; Yu, W.; Moore, A. J.; Zhou, L.; Bayley, P. M.; Kim, G.; Grey, C. P. Cycling Li-O₂ Batteries Via LiOH Formation and Decomposition. *Science* **2015**, *350*, 530–533.
 - (30) Yang, L.; Frith, J. T.; Garcia-Araez, N.; Owen, J. R. A New Method to Prevent Degradation of Lithium-Oxygen Batteries: Reduction of Superoxide by Viologen. *Chem. Commun.* **2015**, *51*, 1705–1708.
 - (31) Matsuda, S.; Hashimoto, K.; Nakanishi, S. Efficient Li₂O₂ Formation via Aprotic Oxygen Reduction Reaction Mediated by Quinone Derivatives. *J. Phys. Chem. C* **2014**, *118*, 18397–18400.
 - (32) Tesio, A. Y.; Blasi, D.; Olivares-Marín, M.; Ratera, I.; Tonti, D.; Veciana, J. Organic Radicals for the Enhancement of Oxygen Reduction Reaction in Li-O₂ Batteries. *Chem. Commun.* **2015**, *51*, 17623–17626.
 - (33) Ren, X.; Lau, K. C.; Yu, M.; Bi, X.; Kreidler, E.; Curtiss, L. A.; Wu, Y. Understanding Side Reactions in K-O₂ Batteries for Improved Cycle Life. *ACS Appl. Mater. Interfaces* **2014**, *6*, 19299–19307.
 - (34) Zhai, D.; Lau, C.; Wang, H.; Wen, J.; Miller, D. J.; Kang, F.; Li, B.; Zavadil, K.; Curtiss, L. A. The Effect of Potassium Impurities Deliberately Introduced into Activated Carbon

- Cathodes on the Performance of Lithium – Oxygen Batteries. *ChemSusChem* **2016**, *8*, 4235–4241.
- (35) Lee, C. K.; Park, Y. CsI as Multifunctional Redox Mediator for Enhanced Li-Air Batteries. *J. ACS Appl. Mater. Interfaces* **2016**, *8*, 8561–8567.
- (36) Ding, F.; Xu, W.; Graff, G. L.; Zhang, J.; Sushko, M. L.; Chen, X.; Shao, Y.; Engelhard, M. H.; Nie, Z.; Xiao, J.; et al. Dendrite-Free Lithium Deposition Via Self-Healing Electrostatic Shield Mechanism. *J. Am. Chem. Soc.* **2013**, *135*, 4450–4456.
- (37) Bender, C. L.; Hartmann, P.; Vrac, M.; Janek, J. On the Thermodynamics, the Role of the Carbon Cathode, and the Cycle Life of the Sodium Superoxide. *Adv. Energy Mater.* **2014**, *4*, 1301863.
- (38) Olivares-Marín, M.; Palomino, P.; Amarilla, J. M.; Enciso, E.; Tonti, D. Effects of Architecture on the Electrochemistry of Binder-Free Inverse Opal Carbons as Li–Air Cathodes in an Ionic Liquid-Based Electrolyte *J. Mater. Chem. A* **2013**, *1*, 14270–14279.
- (39) Pereiro, E.; Nicolas, J.; Ferrer, S.; Howells, M. A Soft X-ray Beamline for Transmission X-Ray Microscopy at ALBA. *J. Synchrotron Radiat.* **2009**, *16*, 505–512.
- (40) Sorrentino, A.; Nicolás, J.; Valcárcel, R.; Chichón, F. J.; Rosanes, M.; Avila, J.; Tkachuk, A.; Irwin, J.; Ferrer, S.; Pereiro, E. MISTRAL: A Transmission Soft X-Ray Microscopy Beamline for Cryo Nano-Tomography of Biological Samples and Magnetic Domains Imaging. *J. Synchrotron Radiat.* **2015**, *22*, 1112–1117.
- (41) Zhai, D.; Lau, K. C.; Wang, H. H.; Wen, J.; Miller, D. J.; Lu, J.; Kang, F.; Li, B.; Yang, W.; Gao, J.; et al. Interfacial Effects on Lithium Superoxide Disproportionation in Li-O₂ Batteries. *Nano Lett.* **2015**, *12*, 1041–1046.
- (42) *Handbook of Chemistry and Physics*, Haynes, W. M. 97th ed.; CRC Press: Boca Raton: FL, U.S.A.; 2016.
- (43) Landa-Medrano, I.; Olivares-Marín, M.; Pinedo, R.; Ruiz de Larramendi, I.; Rojo, T.; Tonti, D. Operando UV-Visible Spectroscopy Evidence of the Reactions of Iodide as

- Redox Mediator in Li – O₂ Batteries. *Electrochem. Commun.* **2015**, 59, 24–27.
- (44) Zhang, T.; Liao, K.; He, P.; Zhou, H. A Self-Defense Redox Mediator for Efficient Lithium–O₂ Batteries. *Energy Environ. Sci.* **2016**, 9, 1024–1030.
- (45) Olivares-Marín, M.; Sorrentino, A.; Lee, R.-C.; Pereiro, E.; Wu, N.-L.; Tonti, D. Spatial Distributions of Discharged Products of Lithium-Oxygen Batteries Revealed by Synchrotron X-ray Transmission Microscopy *Nano Lett.* **2015**, 15, 6932–6938.
- (46) Gallant, B. M.; Kwabi, D. G.; Mitchell, R. R.; Zhou, J.; Thompson, C. V; Shao-Horn, Y. Influence of Li₂O₂ Morphology on Oxygen Reduction and Evolution Kinetics in Li-O₂ Batteries. *Energy Environ. Sci.* **2013**, 6, 2518–2528.

TOC Graphic