XPS Study of the Interface Evolution of Carbonaceous Electrodes for Li-O2 Batteries during the 1st Cycle

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The surface chemistry of the commonly employed positive electrode substrate Super C65 carbon was investigated during the 1st cycle of a Li-O2 battery with a typical ether electrolyte (0.2 M LiTFSI in Diglyme) by performing in situ online electrochemical mass spectrometry (OMES), ex situ scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS). During discharge, a nanometer-thin (< 5 nm) layer of Li2O2 forms homogeneously throughout the electrode before it is passivated at a final specific charge of ~365 mAh/g. Higher discharge charge rates lead to thinner and more densely packed layers of Li2O2. Electrolyte decomposition also occurs in parallel, as evidenced by the continuous increase of LiF and sulfur containing species of the degraded LiTFSI salt. On charge, O2 evolves initially according to a 2e-/O2 rate, but as the cell over-potentials increase, O2 evolution rate approaches 4e-/O2, thus demonstrating a significant extent of parasitic side-reactions. Unlike the discharge, the charge leads to inhomogeneous electrode reactions causing a continuous removal of Li2O2 with no indication of LiO2 or Li2O intermediates. The decomposition side-products formed during discharge are also removed and the spectra of the pristine electrode are nearly retained at a full charge. Our results show that the analysis of Li-O2 battery chemistry requires broad approach based on the combination of various electrode surface sensitive techniques, such as XPS and OMS, in order to provide further fundamental understanding of the mechanisms behind the complex electrochemistry involving the Li and O2 as well as several other predominant degradation products of the electrode and electrolyte.

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Non-aqueous electrolyte based Li-O2 batteries have been a subject of intensive research during the past years, mainly because of their high theoretical specific charge (~1100 mAh/gLi2O2), which provide promising prospects for their implementation in future energy storage systems.1 Several challenges do however remain, of which the most notable are the low round-trip efficiency and poor cycling performance, both partly related to the electrode/electrolyte instability.2−3 On discharge of the Li-O2 cell, gaseous oxygen dissolves in the electrolyte and is reduced at the positive porous electrode where it combines with Li+ (from the negative Li metal electrode) to form solid Li2O2 deposits according to forward reaction of 2Li+ + O2 ↔ Li2O2. Upon charge, the reaction is reversed to release the initial reactants Li+ and O2 gas. Despite extensive research on several classes of electrodes and electrolytes (including carbons, gold, carbides, oxides substrates combined with carbonate, sulfoxide,4−6 nitrile,4,5,7 amide, ionic liquid4,9 or ether10−13 based electrolytes,4,5,7) no composition has so far displayed sufficient chemical stability toward the reduced oxygen species to sustain a satisfactory number of discharge/charge cycles.2 The cell failure has been attributed to the gradual degradation of the electrolyte, which in turn leads to the passivation of the electroactive electrode area by solid side-products.14 Although the detailed mechanisms of the parasitic side-reactions remain unclear, both the electrode and electrolyte solvent/salt have been demonstrated to partially react irreversibly with Li2O2 during cycling to form more thermodynamically stable side-products, such as H2O, CO2, Li2CO3, LiF, R-CHO species, etc.1

In order to address the chemical instability of the various cell components, advanced characterization techniques of complementary nature are required considering the complex chemistry of gaseous, liquid and solid reaction products. Online electrochemical mass spectrometry (OMES) is widely used to analyze gases being consumed and released upon cycling; more particularly in the case of Li-O2 batteries the quantitative detection of O2 gas allows for the determination of the volatile side-reaction products and cell rechargeability.4,14−16 X-ray Photoelectron Spectroscopy (XPS) is a powerful technique suitable to study the extreme surface of materials (analysis depth ~ 5−10 nm) and is used in the field of batteries to study the evolution of electrode interfaces upon cycling. For example, Younesi et al. reported the formation of carbonate and ether containing species on carbon electrode when cycling Li-O2 batteries containing carbonate-based electrodes.20 The chemical composition of the interface may further be semi-quantitatively evaluated, thus permitting a comparison between electrodes recovered after different cycling conditions.

The aim is to study the complex surface electrochemistry of one of the most typical positive electrode material (nanoparticulate carbon Super C65) and electrolyte (0.2 M LiTFSI in Diglyme) combinations for Li-O2 batteries by performing in situ gaseous, ex situ structural, morphological and compositional analysis during the first discharge/charge cycle.

Experimental

Carbonaceous electrode preparation.—The electrodes were prepared by mixing 85 wt% of amorphous carbon Super C65 (Imerys Graphite & Carbon Switzerland) with 15 wt% polytetrafluoroethylene (PTFE) (Sigma Aldrich) binder in a solution of isopropanol and water (1:1) to form a viscous slurry. The slurry was sonicated and kept under mechanical stirring at 100 °C until evaporation of the solvents and formation of a “dough-like” paste. Electrode sheets were obtained by working the dough with a spatula and mechanical rolling (thickness 200 μm). Electrodes were subsequently punched (18 mm diameter, ~12 mg) and dried (120 °C under dynamic vacuum) before being introduced into an Ar-filled glove-box.

Electrochemical cycling.—The electrochemical cycling was performed in a PSI Li-air cell,21 in which an 18 mm diameter lithium metal electrode is wetted with 50 μL of electrolyte (0.2 M LiTFSI in diglyme) and 2 layers of Celgard 2400 separators (28 mm diameter)

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Manuscript submitted July 18, 2016; revised manuscript received August 16, 2016. Published September 16, 2016; publisher error corrected September 28, 2016.
are placed on top. Another 50 μL of electrolyte wets again the separators before the porous carbonaceous electrode is added, which in turn is also soaked with 50 μL of electrolyte. The cells are closed, either directly connected to high purity O2 gas line or connected to the online electrochemical mass spectrometry setup for in situ gas analysis. The cells were equilibrated for one hour before galvanostatic cycling (0.1 mA/cm², referring to the geometric electrode area) between 2.0 and 4.7 V. All potentials are referenced to metallic lithium (vs. Li+/Li). The water content of the electrolyte, as checked by Karl-Fischer titration, was < 10 ppm. The OEMS configuration has been described elsewhere.22 Briefly, the OEMS setup operates with a quadrupole mass spectrometer (MS, QMS 200, Pfeiffer PrismaTM, Germany) for partial pressure measurements, a pressure transducer (PS, PAA-33X, Keller Druck AG, Switzerland) for cell pressure, temperature and internal volume determination, stainless steel pipes and Swagelok fittings (3 mm compression tube fittings, Swagelok, OH, US) to connect the OEMS cell, a set of solenoid valves (2-way magnetic valve, Type 6126, EPDM seal, Christian Bürkeritz GmbH & Co, Germany) and a membrane pump (Edwards E2M30 oil pump, EDWARDS GmbH, Germany) for efficient flushing. O2 consumption during discharge was monitored with the pressure transducer. Before charge, the cells were step-wise flushed (10 min time intervals) with Ar until the amount of oxygen detected in the mass spectrometer approached base-line levels. During charge, the magnetic valves were automatically opened/closed with a Solid State Relay Module (NI 9485 measurement System, National Instruments, TX, US) connected to a LabView Software (NI Labview 2012, National Instruments, TX, US) in order to probe the partial pressures of O2 (m/z = 32) and CO2 (m/z = 44) of the cell. For each measurement point, 0.7 mL of gas is extracted from the headspace (3.2 mL) of the cell for partial pressure analysis and replaced by pure Ar (Quality 6.0). Gas evolution rates were calculated on the basis of Scofield’s relative sensitivity factors. The pressure in the analysis chamber was monitored with the pressure transducer. Before charge, the cells were step-wise flushed (10 min time intervals) with Ar until the amount of oxygen detected in the mass spectrometer approached base-line levels. When the pattern is compared to those collected for reference compounds, which could be expected upon charge for an ether based electrolyte [e.g. (3) Li2O2H, (4) LiCO2CH3, (5) LiOH · H2O, (6) Li2O, (7) Li2CO3 and (8) Li2O2], dashed lines are guides for the eye.

Results and Discussion

Structural characterization of discharge products.—After the discharge, the Li2O2 cell containing a porous Super C65 electrode was dismantled in an Ar-filled glove-box and the porous electrode washed with diglyme. The dried porous electrode was then cut into small pieces that were either introduced inside a 0.5 mm glass capillary for X-ray diffraction analysis or mounted on a carbon tape stub for scanning electron microscopy (SEM, Ultra 55, Zeiss, Germany). The capillaries were sealed with wax before being taken out of the glove-box. The synchrotron X-ray diffraction experiments were performed at the Villigen at a wavelength of 0.708965 Å. The data acquisition was 2 min. In order to assess the nature of the crystalline species present in the porous electrode, data were also collected for reference materials. The SEM stubs were transferred to the analysis chamber of the microscope under inert atmosphere and micrographs were made at beam energy of 1 kV.

X-Ray Photoelectron Spectroscopy.—XPS measurements were carried out on a VG ESCALAB 220iXL spectrometer using a focused monochromatized Al Kα radiation (hv: 1486.6 eV, spot diameter 500 μm). The pressure in the analysis chamber was ~ 5.10−9 mbar. The spectrometer was calibrated using the photoemission line Ag 3d5/2 (binding energy 368.3 eV). Core peaks were recorded with a constant 30 eV pass energy. The binding energy scale was calibrated using the major carbon contribution (Super C65). No flood gun neutralization was applied due to the good conductivity of the carbonaceous electrodes. Core peaks were analyzed using a non-linear background Shirley-type background. The peak positions and areas were optimized by a weighted least-square fitting method using 70% Gaussian, 30% Lorentzian line shapes. Quantification was performed on the basis of Scofield’s relative sensitivity factors. The samples were transferred to the XPS introduction chamber in a hermetically sealed transfer chamber to avoid any air contamination. In order to evaluate the impact of the washing on the chemical composition of the interface layer on the porous electrode, XPS data were collected on washed and unwashed samples after a blank experiment and after the 1st discharge. Before the washing, the analyzed electrode was cut into halves. One half remained unwashed while the other half was washed with diglyme. The main component of the C 1s spectra is that of the pure carbons (284.3 eV, mainly sp 2 carbons) and was chosen for calibration as it could be easily deconvoluted and presents narrow FWHM (~ 0.8).

Figure 1. SEM micrographs of (a) pristine, (b) discharged and (c) charged C65 electrodes (0.1 mA cm−2). White scale bar corresponds to 1 μm. (d) X-ray diffraction of (1) discharged and (2) pristine electrodes as well as reference powders of (3) Li2O2H, (4) LiCO2CH3, (5) LiOH · H2O, (6) Li2O, (7) Li2CO3 and (8) Li2O2. Dashed lines are guides for the eye.

Structural characterization.—Figure 1a–1c shows a SEM micrograph of the pristine, discharged and charged C65 electrode, respectively. The pristine C65 electrode consists of nanometric spherical particles aggregated in micron-sized clusters forming an open and well-connected inter-particle pore network. After discharge (Fig. 1b, ~365 mAh/g), the integrity of the particle and pore network is preserved, although the presence of a thin precipitate on the C65 carbon may be anticipated. Based on the resolution of the SEM micrographs, a less than 10 nm thick deposit appears to have formed with no sign of larger toroidal-shaped particles, in accordance with previously reported data at comparable current densities (0.1 mA/cm² geometric surface area ~ 0.46 mA/m²).23 Upon charge, the morphology of the pristine electrode is retained, thus supporting the notion that the discharge/charge chemistry solely involves formation/dissolution of nanometer-thin surface deposits without any major structural changes imposed on the carbonaceous electrode. Figure 1d shows the X-ray diffractogram of the (1) discharged and (2) pristine C65 electrodes along with (3–8) reference powders. Apart from broad bumps at 2θ = 12°, 21° and 34°, no peaks were seen for the pristine electrode consisting of amorphous C65 carbon and the PTFE binder. At the end of the 1st discharge, additional low intense peaks are visible at 2θ = 14.9, 15.9 and 26.1°. When the pattern is compared to those collected for reference compounds, which could be expected upon discharge for an ether based electrolyte [e.g. (3) Li2O2H, (4) LiCO2CH3, (5) LiOH · H2O, (6) Li2O, (7) Li2CO3 and (8) Li2O2], the peaks of the discharged electrodes correspond to Li2O2 that is confirmed to be the major crystalline discharge product.
Minor peaks at $2\Theta = 14.4$ and $16.8^\circ$ may indicate also the presence of Li$_2$O, however most probably formed as an artifact during the intense synchrotron irradiation.\cite{24} In conclusion, judging from the SEM micrographs and XRD diffractograms, aside from nano-sized Li$_2$O$_2$ crystallites, any available discharge products formed on Super C65 carbon would be in the form of mostly amorphous nanometer-thin layer. Therefore, complementary characterization techniques, such as XPS, are required to investigate the formed products.

**Discharge.—** Figure 2a shows the potential profile of the first discharge/charge cycle. During discharge, a single plateau $\sim 2.6$ V is observed before the cutoff potential ($\sim 2$ V, $\sim 365$ mAh/g) is reached. The O$_2$ consumption (in mmol/min, Figure 2b) was calculated by recording the gradual reduction of cell pressure during discharge. Based on the applied current (0.1 mA/cm$^2$), an average consumption rate of $2.06e^{-}/O_2$ is observed, which is close to what would be expected for the formation of Li$_2$O$_2$ ($2e^{-}/O_2$), although the slight deviation indicates the presence of side-reactions during discharge.\cite{17}

**Ex-situ** XPS analysis of electrodes from identically prepared and used pristine electrodes, without any contact with the electrolyte, are dominated by the carbon C-C peak ($\sim 62$ at%, Figure 2c) in the C 1s spectrum and by the peak corresponding to the PTFE binder in the F 1s spectrum ($\sim 8$ at%, Figure 3). The presence of the binder is also discernible by the small component at $\sim 292$ eV attributed to $-CF_2$ groups. Other minor components at $\sim 285.2$ and $\sim 286.3$ eV result from the presence of adventitious species adsorbed at the surface of the electrodes. The bump visible at higher binding energies $\sim 692$ eV (F 1s, Figure 3) is probably an experimental artifact related to a local charging effect of the binder during analysis due to its low electrical conductivity. The noisy O 1s spectra of the pristine electrode indicate a low amount of adsorbed oxygenated species at the surface ($< 2$ at%). Neither Li nor S containing species were detected on the pristine electrode.

Blank electrodes (0 mAh/g, Figure 2c) were recovered from the cells after being kept under O$_2$ atmosphere at open circuit potential ($\sim 3.1$ V) for a time period comparable to a typical discharge. Although the overall signal intensity of the C-C peak reduced to $\sim 45\%$, the C 1s spectral features are similar to those of the pristine electrode. The intensity of the components related to CH$_x$ ($\sim 285.3$ eV) and CO$_x$ ($x = 1$: $\sim 286.5$ eV, $x = 2$: $\sim 289.0$ eV, and $x = 3$: $\sim 289.5$ eV) environments in the C 1s spectrum (Blank, Figure 3) are slightly pronounced, which most probably is related to the presence of electrolyte remaining strongly adsorbed to the amorphous carbon electrode. A chemical modification of the surface through a reaction with the electrolyte containing dissolved O$_2$ can’t however be excluded. On the O 1s spectrum of Blank, distinct contributions at 532.4 and 533.6 eV are observed and likewise attributed to an increased presence of CO$_x$ species associated with adsorbed electrolyte. However, when comparing the respective spectra of the washed Blank, unwashed Blank and pristine electrodes (Figure 3), new components at $\sim 534$ eV (O 1s spectrum), $\sim 170.6$ eV and $\sim 169.4$ eV (S 2p spectrum, doublet due to spin-orbit coupling) attributed to the SO$_2$ groups as well as peak at $\sim 293$ eV (C 1s spectrum) attributed to the $-CF_2$ groups of the LiTFSI salt residue are identifiable for all electrodes contacted by the electrolyte.\cite{28,32} Therefore, in order to account for the electrolyte salt (as well as insoluble/soluble electrochemical reaction products) on the electrode surface after drying, the electrodes were separated into a washed (in pure diglyme) and an unwashed part prior to analysis. However, the strong contribution of the LiTFSI salt and the diglyme solvent to the global signal attenuated the intensity of several minor species and all analyzed electrodes were washed before XPS characterization. Despite thorough washing, salt and electrolyte residues were always present and partly obscured the signal intensities on C 1s, O 1s and S 2p spectra. On the F 1s spectrum, the PTFE contribution remains the main component of the Blank electrodes, but a second component with binding energy $\sim 691.5$ eV is also visible, and it is not yet clear to which species such a component may be related: adsorbed SF$_6$ species, higher binding energies of $\sim 692.7$ eV\cite{31} and C$_6$F$_6$, C$_6$H$_4$CF$_3$, C$_6$HF$_3$ have lower binding energies of $\sim 690.9$\cite{27}, $\sim 690.8$\cite{35} and $\sim 697.0$ eV\cite{34} respectively. No signal intensity was recorded at the Li 1s spectrum ($\sim 52$–$59$ eV) prior to discharge.

During discharge, the Li$^+/Li$ and O$^/-O_2$ components increased monotonically (Figure 2c) with a Li$^+/Li$ $\sim 1$ confirming the gradual increase of Li$_2$O$_2$ on the surface, which was expected from the constant O$_2$ gas consumption rate of $\sim$Li$_2$O$_2$ (Figure 2b). Interestingly, the surface composition of the gas- and separator-facing sides of the electrode (e.g. compare solid/hollow symbols) are nearly identical, thus providing support for the homogenous formation of a conformal layer of reduction products throughout the electrode, as suggested by McCloskey et al.\cite{1} In addition, no sign of inhomogeneous growth of Li$_2$O$_2$ in the electrodes was observed by SEM. While the Li 1s spectra only contained a single component (associated with Li$_2$O$_2$ at $\sim 55$ eV, Figure 3), the O 1s spectra displayed apart from the Li$_2$O$_2$ at $531.7$ eV\cite{29,32,35} at least 2 components $\sim 532$ eV, which slightly increased in intensity during discharge. These components (533 and 534 eV, which can be assigned to SO$_2$ and CO$_x$ and CO$_3$, respectively)\cite{28,36} are believed to mainly result from presence of adsorbed electrolyte residues on the formed Li$_2$O$_2$. The insufficient removal of adsorbed species unfortunately obstructs a clear identification of the origin of signal intensity at higher binding energies than $532$ eV on the O 1s spectrum during the whole cycle.

During discharge, the C-C peak contribution to the over-all signal intensity consistently decreases from 45% (Blank) down to 15%
Figure 3. F 1s, O 1s, C 1s, S 2p and Li 1s XPS spectra for the pristine C65-based electrode and washed electrodes extracted from Li-O2 cells partially discharged (100, 200 mAh/g), fully discharged, partially charged (75, 220, 365 mAh/g) and fully charged. For comparison XPS spectra for washed and unwashed electrodes recovered from an uncycled blank cell are also plotted.

(full discharge) due to the increasing, but thin (< 5 nm, according to the XPS analysis depth) thickness of Li2O2 covering the carbon substrate (Figure 2c). Interestingly, cells discharged at a higher current density of 0.3 mA/cm2 achieved a lower specific charge (~220 mAh/g), but the same electrode surface composition of Li2O2 ~ 16 at% compared to a cell discharged at 0.1 mA/cm2 to the same specific discharge. However, the C-C contribution to the over-all signal was significantly higher. A higher current density thus leads to the same amount of Li2O2 (in atom% corresponding to 2e-/O2), but in the form of thinner layers before the electrode is passivated. The latter finding confirms the claims of previous studies,1,23 showing that in the absence of a redox mediator in the electrolyte (e.g. H2O, NO3, I-/I3 etc.) only a nanometer thin layer of Li2O2 is homogeneously formed throughout the electrode at end of discharge. The C-C peak remains the main component of the C 1s spectrum (Figure 3) during discharge, although signal intensities associated with CHx and COx (x = 1,2,3) environments are present at all steps of the discharge. However, their contributions to the over-all signal are roughly constant during discharge (≈ 5 at% not plotted) and are to a large extent associated with adsorbed electrolyte, thus obstructing any conclusive evidence of decomposed electrolyte on the Li2O2 surface. Previous studies based on FTIR and 1H NMR techniques to analyze discharged Super P electrodes in ether-based electrolytes identified HCO2Li, CH3CO2Li, Li2CO3 and possibly polyethers/esters as electrolyte decomposition products upon cell discharge.3

Nevertheless, electrolyte decomposition is here clearly observed during the whole discharge process, as is evident from monotonic increase of the average signal intensity associated with LiF (684.7 eV, Figure 3).27 PTFE based binders are fully fluorinated and already widely reported to be chemically stable toward Li2O2.38 In addition, several previous studies demonstrated the presence of LiF solely when fluorinated salts were available, such as LiTFSI,39 thus supporting our assumption that LiF originates from LiTFSI salt and not the PTFE binder. Furthermore, the degradation of the LiTFSI salt is also observed on the S 2p spectrum with the formation of double split peaks at ~167.3 eV and ~168.5 eV, most probably related to salt decomposition products formed during the last stages of discharge. Apart from the main component at ~689.1 eV of the PTFE on the F 1s spectrum, the unknown high binding energy component at ~692 eV is persistent.

Charge.—The charge onset cell voltage is 3 V where O2 initially appears to evolve at a rate ≈ 2e-/O2 as expected for Li2O2 oxidation (Figure 2a, 2b). Li2O2 is the only discharge product that has been confirmed to return O2 during oxidation.40 However, as the charge overpotential increases, O2 evolution gradually drops < 2e-/O2, clearly demonstrating the presence of side-reactions during the whole charge process. The OEMS data largely agrees with observations of McGloskey et al.1

Ex-situ XPS analysis was performed on electrodes collected at various stages of charge (75, 220 and 365 mAh/g) and at the cutoff voltage of 4.7 V at the end of charge (540 mAh/g). During charge, the Li+ and O− signal intensity monotonically decreases, however while maintaining a ratio of Li+ /O− ≈ 1, thus confirming the gradual decomposition of Li2O2 (Figure 2c) without any evidence of other lithiated oxide or superoxide phases (Li2O or LiO2). Interestingly, at 75 mAh/g the electrode surface composition of Li+ and O− on the separator side of the electrode is markedly higher (~18 at%, hollow symbols) compared to the electrode surface facing the gas head-space (~14 at%, solid symbols). A similar difference between the two electrode sides is equally found at a later stage of charge (~220 mAh/g), which could be explained by facilitated mass transport (e.g. O2) during oxidation of Li2O2 close to the O2 gas cell headspace. For instance, O2 gas bubble formation inside the electrode may partly obstruct diffusion of O2 in the electrode, thus resulting in inhomogeneous reactions where Li2O2 in regions close to the gas headspace are more easily oxidized due to the facilitated mass transport.

At the specific charge of 365 mAh/g (roughly corresponding to the obtained discharge capacity), the signal intensities related to Li2O2 are nearly diminished (Figure 2c), but O2 continues to evolve at a rate of ~4e-/O2, which again may be explained by inhomogeneous electrode reactions where Li2O2 at the outer surfaces of the electrode oxidizes early. Alternatively, remaining Li2O2 nanoparticles may at this stage be covered by electrolyte decomposition products as significant cell over-potentials are necessary for carbonate/carboxylate oxidation (i.e. CO2 evolution starts at ~4V, Figure 2b) are required to support further O2 evolution.

Further support for increased influence of electrolyte degradation products is discernable in Li 1s spectra of Figure 3, where a second component at 56 eV grows in intensity during charge, which we relate to a lithium carbonate Li2CO3 (Figure 2c). But the presence of other
lithiated compounds, such as lithium acetate, can’t be excluded according to previous observations. The evolution of O$_2$ drastically drops after the potential plateau at ∼4.2 V, whereby CO$_2$ evolution takes over as the major evolving gas. The fact that CO$_2$ derives from oxidation of earlier formed electrolyte decomposition products is apparent as the CO$_2$ evolution rate drops after the potential plateau at ∼4.5 V. Above 4.5 V, the direct anodic oxidation of the diglyme ether is expected, which does not result in formation of CO$_2$. Additional evidence of the removal of the lithiated carbonate/carboxylate species >4V is given by the absence of lithiated compounds on the Li 1s spectrum at the end of charge (Charged, Figure 3). Charging at a higher rate (0.3 mA/cm$^2$) results in incomplete oxidation of both Li$_2$O$_2$ (∼8 at%) and electrolyte decomposition products, which supports the explanation of mass transport limited reactions.

Apart from the diminishing signal at 531.7 eV related to Li$_2$O$_2$ on the O 1s spectrum, there is an evolution of at least two more components >532 eV, which again most probably are overlapping signals from adsorbed and decomposed electrolyte species (e.g., carbonates (∼532eV),) carboxylates or poly-ether polymers. The same conclusion can be made while inspecting the C 1s spectrum, which displays the presence a wide range of species, such as CO$_2$, and CH$_x$ (e.g., ethers or carbonates). The CH$_x$ component is particularly strong in the presence of Li$_2$O$_2$, indicating a strong adsorption/reaction with the discharge product.

Interestingly, the decomposition products of the salt (S 2p$_3/2$ ∼ 167.2 eV on the S 2p spectrum) and LiF (component at 684.8 eV on the F 1s spectrum), which were mainly formed during the discharge, gradually disappear during charge. For instance, no LiF is found after a complete charge to 4.7 V (Figure 2c). These decomposition products may dissolve, presumably assisted by the organic decomposition products formed during charge. The component centered at ∼691.5 eV also disappears on full charge and the F 1s spectrum of the pristine electrode is retrieved with the main component of the PTFE binder (∼689.2 eV) remaining unchanged, in accordance with previous studies.

Conclusions

The surface chemistry of the commonly employed positive electrode substrate Super C65 carbon was investigated during the 1st cycle of a Li$_2$O$_2$ battery with a typical ether electrolyte (0.2 M LiTFSI in Diglyme). During discharge, structural characterization evidenced the continuous formation of nano-crystalline thin layer of Li$_2$O$_2$, which according to OEMS and XPS continuously forms homogeneously throughout the electrode (thickness < 5 nm) before the electrode is passivated. Higher discharge charge rates leads to thinner and more densely packed layers of Li$_2$O$_2$. Electrolyte decomposition also occurs in parallel, as evidenced by the continuous increase of LiF and electrolyte decomposition products, which supports the explanation of mass transport limited reactions.

On full charge, the spectra of the pristine electrode are nearly retained, thus demonstrating that all electrochemically deposited products are apparently removed.

Acknowledgment

Funding of PSI by BASF SE is gratefully acknowledged. The authors would also like to thank Dr. Mario El Kazzi for technical assistance with the XPS instrument.

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Publisher’s Note: XPS Study of the Interface Evolution of Carbonaceous Electrodes for Li-O₂ Batteries during the 1st Cycle \textit{[J. Electrochem. Soc., 163, A2545 (2016)]}

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This article was originally published on August 16, 2016, with the last author’s first name missing on page A2545. ECS apologizes for this error. The article was corrected online on September 28, 2016.