Degradation and stabilization of lithium cobalt oxide in aqueous electrolytes†

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We report herein the exceptional cycle stability of lithium cobalt oxide (LCO) in aqueous electrolytes of high lithium salt concentrations. We demonstrate retention of up to 87% of the initial discharge capacity after 1500 cycles at a 1C charge–discharge rate. We also demonstrate that LCO, when in contact with each of the aqueous electrolytes tested, exhibits a high electrode potential and a large initial discharge capacity, similar to that of LCO electrochemically cycled in conventional organic electrolytes. More importantly, our systematic studies and post-mortem analyses of LCO cells reveal that the primary mechanism of LCO degradation in aqueous electrolytes is the formation of a resistive layer of cobalt(II) oxide on the particles’ surfaces. We show that higher electrolyte molarity and certain salt compositions may significantly reduce the layer thickness and dramatically improve LCO stability. These findings constitute a substantial step towards development of gravimetrically and volumetrically energy dense aqueous lithium ion batteries.

Broader context

Lithium-ion batteries (LIBs) with aqueous electrolytes are significantly safer, more environmentally benign and potentially cheaper than traditional LIBs comprising organic electrolytes. Higher ionic mobilities for the Li+ ions in aqueous electrolyte solutions give more power and allow significantly faster charging of aqueous batteries. Such characteristics are highly desired for growing energy storage applications, including energy storage for electric vehicles and electrical grids increasingly reliant upon intermittent clean and renewable sources of energy. Lithium cobalt oxide (LCO) remains the dominant cathode material in commercial LIBs used in electronic devices. It has been known to degrade in aqueous environments, but the origins of such a degradation remain unclear. Here we uncover the key degradation mechanisms of LCO in aqueous electrolytes. More importantly, we reveal an opportunity to dramatically enhance its electrochemical stability by tuning the composition and increasing the concentration of low-cost lithium salts in aqueous electrolytes. The demonstrated 87% capacity retention in LCO after over 1500 charging and discharging cycles is unprecedented. The obtained results will contribute to the progress in the broad field of aqueous metal-ion batteries.

Introduction

John Goodenough et al. pioneered the use of lithium cobalt oxide (LCO) as a unique lithium ion battery (LIB) cathode material.1 Following Goodenough’s work, LCO was commercially produced and successfully utilized in a majority of LIBs by multiple companies. Widespread use of LCO is owed in part to its high volumetric capacity (1363 mA h cm⁻³), high discharge potential (approx. 3.93 V vs. Li/Li⁺), and long cycle life.1,2 Low thermal stability and faster degradation at higher currents remain downsides for the use of LCO in today’s commercial LIBs.2 The propensity for LCO to decompose in an exothermic reaction that releases oxygen, in combination with highly flammable organic electrolytes, adds a significant safety risk to the use of LCO-based LIBs.3 As a result, safety measures often require overbuilding battery management systems (battery packs) with inactive materials, which increase the weight, volume and cost of the energy storage by up to 75% in the case of cell applications in large batteries, such as electric vehicles.4 To date, non-aqueous electrolytes have been the electrolytes of choice for LIBs5 because of their high stability in a broad potential range, which enables LIB operation at voltages of up to around 4.4 V. Minor decomposition of organic electrolytes at the surfaces of anodes and cathodes typically leads to the formation of stable solid surface layers known as solid–electrolyte interphases (SEIs).6 SEI may help stabilize the performance of electrodes over a large number of cycles and prevent further electrolyte decomposition.

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In comparison, water electrolyzes at a much lower potential difference, with a thermodynamically stable window of approximately 1.23 V when not considering the impact of a dissolved salt. Thus, it was believed that constructing a LIB with an aqueous electrolyte should require choosing a cathode and an anode of only moderately high and low electrode potentials, respectively, limiting the battery to a lower voltage (and thus lower energy density). It was not until the mid-1990s that W. Li et al. published one of the first papers on LIBs in aqueous electrolytes. Although the battery operated with a relatively low voltage of approximately 1.5 V (average) and showed a moderate cycle life (lasting approximately 25 cycles), their important research proved that it was possible to make secondary LIBs with aqueous electrolyte solutions. In order to improve safety, environmental friendliness, and rate capability of LIBs, a renewed interest in gaining better understanding of the behavior of LIB materials in aqueous electrolytes has recently emerged. Indeed, aqueous electrolytes offer safe, inexpensive, environmentally friendly, and highly ionically-conductive alternatives to organic electrolytes. They may allow using thicker and less-expensive-to-manufacture electrodes and significantly reduce the dependence on battery management systems. Several methodologies may be utilized for increasing cell voltage, such as exploring over-potentials for oxygen evolution on the cathode and hydrogen evolution on the anode, utilizing a combination of solid and aqueous electrolytes, and, as most recently shown, forming an SEI. A variety of commercial cathode materials used in today’s commercial LIBs (LiFePO4 (LFP), LCO, LiNi0.5Co0.2Mn0.3O2 (NMC), LiMnO2 (LMO), etc.) have been preliminarily studied in combination with aqueous electrolytes. However, in contact with aqueous electrolytes, such materials typically exhibit poor electrochemical performance and short cycle life. When a detailed understanding of the electrode and ALIB degradation phenomena is still mostly lacking, several factors have recently been proposed to impact cell stability, such as electrolyte pH and dissolved oxygen content. Dissolution of the active material, intercalation of H+ ions into the active material alongside Li+ ions, and reactions between the active material and dissolved O2 and H2O. In our recent studies on the electrochemical cycling of LFP cathodes in aqueous solutions, we identified that side reactions occurring between LFP particles and water molecules induce surface dissolution and electrochemical separation of active particles. More importantly, we discovered that increasing the concentration of the lithium salt in the aqueous electrolyte leads to significant reduction of the dissolution reactions and leads to improvements in cycle stability. Inspired by such findings, we investigated the electrochemical behavior of higher voltage LCO in low-cost Li2SO4 or LiNO3-based aqueous electrolytes.

Similar to our previous study, we found that higher salt concentration leads to increased cathode stability. However, in contrast to our prior work, the degradation mechanisms in LCO were found to be markedly different than that in LFP. Instead of electrical separation of active particles, LCO electrodes develop an ionically isolative surface layer, which high concentration electrolytes may prevent building. While some of the electrochemical properties of LCO have been previously investigated, the comprehensive studies of the mechanisms of LCO degradation as well as the impact of salt concentration and composition have not been reported, and ultra-long cycle stability of LCO in aqueous electrolytes has not been achieved before.

Results and discussion

Fig. 1 shows the cyclic voltammograms (CVs) for LCO in aqueous electrolytes of LiNO3 and Li2SO4 salts of varying molarities (1 M, 5 M and 9 M/saturated LiNO3 solution, and 0.5 M, 1 M and 3 M/saturated Li2SO4 solution). These CVs show an oxidation/delithiation peak at approximately 3.94 vs. Li/Li+. A corresponding reduction/re-lithiation peak appears at approximately 3.92 V vs. Li/Li+. These potentials correspond to a Li+ concentration of 1 M in each of the electrolytes. With increasing molarities of electrolytes, there is a corresponding increase in the redox potential of these peaks in accordance with the Nernst equation. These results confirm that our cell construction is robust and LCO is active in aqueous electrolytes.

To understand the charge–discharge (C–D) behavior of LCO in aqueous electrolytes, electrochemical cells were assembled with electrolytes of varying molarities of LiNO3 and Li2SO4 salts, as used in the CV experiments. In order to minimize the impact of the counter electrode (CE) on cell performance, both the working electrode (WE) and CE were constructed with LCO as the active material. The CE was constructed to exhibit a larger capacity loading and was partially delithiated to allow Li+ cycling between the two electrodes (without partially removing Li+ from the CE, the CE would have no storage capacity for Li+ when Li+ is extracted from the WE). A constant current corresponding to a 1C rate of C–D was applied between the WE and CE, with the potential of the WE versus the CE limited to between +0.15 V to –0.2 V (Fig. 2).

A higher concentration of the lithium salt substantially increased the capacity retention for LCO. Interestingly, LCO exhibited more stable cycling in the Li2SO4 solution than in the LiNO3 solution, which is clearly seen in the case of saturated electrolytes or when comparing the capacity retention for lower concentration – 0.5 M Li2SO4 solution and 1 M LiNO3 solution – in
which the Li⁺ concentrations were equal (Fig. 2c and f). Based on the previous findings made by our group while studying LFP cathodes, improvement in discharge capacity retention with higher lithium salt concentration is likely connected to a reduction in the water activity and water-induced undesirable side reactions (to be further discussed), and a corresponding increase in the lithium activity. As a result, LCO maintained a remarkably large part of its capacity (~87%) after 1500 cycles in concentrated Li₂SO₄ electrolyte, which is high even for commercial quality LIBs with organic electrolyte.

Fig. 3 shows changes in the corresponding voltage–capacity plots for the electrochemical cells. We see an increase in the polarization of these cells with cycling, evident from the broadening or separation of the charging and discharging curves with cycling. With the exception of the saturated LiNO₃ electrolyte, this polarization is more prominent for electrochemical cells which degrade faster (such as those constructed with 1 M LiNO₃ electrolyte) than for electrochemical cells that degrade slower (such as those assembled with saturated Li₂SO₄ electrolyte). Higher polarization of the cell with saturated LiNO₃ electrolyte (even when compared to the 5 M LiNO₃ electrolyte cell, compare Fig. 3b and c) is likely related to the observed (visible by eye) recrystallization of LiNO₃ into larger crystals in the electrolyte upon slow water evaporation (our cells were sealed, but were not perfectly hermetical). Such crystals may block electrolyte access, inducing undesirable polarization growth. In contrast, saturated Li₂SO₄ electrolyte does not exhibit this behavior – it tends to precipitate salt crystals at the bottom of the cell due to lower solubility in water and lower solvation energy. As a result, the corresponding cell polarization remains small even after 1500 cycles (Fig. 3f).

Electrochemical impedance spectroscopy (EIS) was performed on the cycled electrodes at regular intervals to gain additional insights into the nature of the degradation of performance (Fig. 4). Fig. 4(a) and (b) show changes in EIS in the worst (1 M LiNO₃) and the best (saturated Li₂SO₄) performing cells. EIS measurements were taken after 1, 30, 100, 250, 500 and 1500 cycles. We see an increase in the overall cell resistance (Z-real) with cycling. We also see a direct correlation between cell capacity fading and cell resistance increase after 500 cycles in all the electrolytes (Fig. 4c and d).
corresponds to a higher degree of degradation, consistent with trends in polarization observed in the C–D tests (Fig. 3).

To identify the changes to the LCO electrodes during cycling we conducted extensive post-mortem analysis using a broad range of surface-sensitive and bulk material characterization techniques. For microstructural imaging at the nanoscale, LCO particles were examined using high resolution Transmission Electron Microscopy (TEM) (Fig. 5). The surfaces of LCO were imaged after cycling electrodes in 1 M LiNO₃ solution (for which there was the largest loss of discharge capacity and greatest rise in impedance) for 500 and 1500 cycles (Fig. 5b and c). The surfaces of uncycled LCO were also imaged as a reference (Fig. 5a). Uncycled LCO powder showed the lack of any surface films and the extension of crystal planes all the way to the particle surfaces (Fig. 5a). On cycling, however, an amorphous layer forms on the surface (no crystal planes were visible). This amorphous surface film increases in thickness with longer cycling (from 5–6 nm in thickness after 500 cycles to 8–10 nm in thickness after 1500 cycles in 1 M LiNO₃). Noticeably thinner surface layers were observed on LCO cycled in the electrolytes that were more stable (e.g., in the case of 0.5 M Li₂SO₄ the thickness was 2–3 nm after 500 cycles). In some areas in 0.5 M Li₂SO₄ electrolyte, crystal planes extended all the way up to the surface, although there was a noticeable change in the crystal plane spacing (as seen in Fig. 5d), suggesting a phase change on the surface layer after 500 cycles. This effect was noticed to lower extents in cells cycled in 1 M and saturated Li₂SO₄ electrolytes where the performance was much more stable. HRTEM image analysis was also conducted to reveal the crystal structure of the layers formed at the surface of the LCO grains after cycling. Fig. 5f shows an example of the nanocrystals formed on the surface of the LCO sample cycled in 0.5 M Li₂SO₄ for 500 cycles. The measured d-spacing values of such nanocrystals match closely 2.46 Å spacing of the (111) planes in CoO, while that of the bulk of the grain match closely the 4.68 Å spacing of the (003) planes in LCO (see ESI: Table 1). The surface chemistry was investigated further with XPS.

X-ray Photo-Electron Spectroscopy (XPS) was conducted on electrodes to investigate the composition of the surface layers detected by TEM. Electrodes cycled in the different electrolytes of varying concentrations were analyzed for changes in surface composition, oxidation state of cobalt, and the stoichiometric ratio of O:Co. A reference sample of pure LCO was also analyzed using the same parameters. Samples were analyzed using a survey scan to measure the ratio of O:Co on the surface. The peak area under the curve for the Co 2p peak and the O 1s peak of the survey scan (same pass energy) were used to measure the atomic ratio of cobalt and oxygen atoms on the surface (see ESI: Fig. 1).

A detailed scan for oxygen 1s revealed the different types of oxygen bonds present on the surface of the particles (see ESI: Fig. 2). Two types of oxygen 1s bonds were observed — one with a peak at approximately 529 eV binding energy, corresponding to
the O–Co bond. The other was at approximately 532 eV binding energy that corresponded to the organic C–O bond from adventitious carbon adsorbed on the surface or carbon additives with functional groups on the surface. Curve fitting was carried out using a linear background fit with the proprietary software from Thermo K-Alpha. Using the fit, the fraction of the O-1s peak that corresponded to the O–Co bond was calculated as the fraction of the total area under the O-1s curve. This fraction was then multiplied with the atomic percentage obtained from the survey scan to obtain the actual contribution of oxygen to the O–Co bond. The ratio of O : Co was then calculated.

As expected, the O : Co ratio was approximately 2 : 1 for a pure LCO sample. However, with cycling, this ratio sequentially decreased and approached closer to 1.5 : 1 (as shown in Fig. 6). This implies that the surface of the LCO is being reduced over time so that the Co(III) ions in LCO are slowly converting to the Co(II) ions with cycling. In other words, the surface composition of LiCo(III)O2 (O : Co = 2 : 1) slowly changed to Co(II)O. This effect was more pronounced in cells that had degraded more (compare, for example, 1 M LiNO₃ versus 1 M Li₂SO₄, Fig. 6). Similar trends were observed in both types of electrolytes (LiNO₃ and Li₂SO₄) suggesting that the phenomenon of Li₂O leaching from the surface leading to the formation of cobalt(II) oxide surface layer (Fig. 5), that correlates to the capacity fading (Fig. 2 and 3) and resistance growth (Fig. 4) in LCO, is somewhat universal (at least for studied aqueous electrolytes) and only differs in magnitude – depending on the electrolyte composition and salt concentration.

Detailed scans on the Co 2p peak were also analyzed for all samples (Fig. 7). It must be mentioned that the binding energy values for all the samples was found to be consistently at ~284.86 eV for the C–C 1s peak (from adventitious carbon) and at ~688.29 eV for the F-1s peak (from PVDF binder), which provided an internal calibration standard for all the samples. The 2p 3/2 peak for Co in pure LCO was used as the reference peak and chemical shift in the cycled samples was studied. We noticed that a peak shift occurred towards lower binding energies (BE) in all samples. A shift towards lower binding energies implies that it is easier to extract an electron from the Co ion. This indicates that the Co ions in the surface layer have a lower oxidation state than originally in LCO, providing additional evidence for the reduction of Co(III) ions to Co(II) state. We also observed that the shift towards lower binding energies was higher with greater degradation of the electrodes. For example, LCO cycled for 1500 cycles in either 1 M LiNO₃ or 0.5 M Li₂SO₄ showed a slightly larger shift than LCO cycled for 500 cycles in these electrolytes. On similar lines, it was also observed that the chemical shift after 500 cycles in more concentrated electrolytes (1 M Li₂SO₄, lower degradation) was even lower than in less concentrated electrolytes (1 M LiNO₃), which is in agreement with the charge–discharge tests (Fig. 2). Fig. 8 summarizes these findings and shows the peak values for BE of the Co 2p 3/2 peak plotted as a function of the percentage degradation in the electrodes. Larger degree of the reduction of Co(III) ions to Co(II) state (thickness of the cobalt oxide layer on the LCO surface) correlates well with the larger degradation of the electrodes.
X-ray diffraction (XRD) analyses were performed on selected LCO samples. Fig. 9 shows the XRD spectra for LCO electrodes cycled in 1 M LiNO₃ electrolyte for different numbers of cycles. The XRD spectra reveal that the LCO crystal structure is still present, with no new crystalline phases appearing, even after cycling for 1500 cycles. This provided additional evidence to support the understanding that the loss of LCO capacity was predominantly a surface phenomenon and no significant changes in the bulk of LCO took place.

SEM images provided further evidence that there was no apparent change in the LCO particle morphology after cycling (Fig. 10). No cracks or noticeable surface roughening could be observed. This insight further supports the lack of significant chemical and structural changes in the bulk of the LCO particles during cycling.

In order to distinguish ionic versus electronic resistance growth mostly responsible for capacity fading, cells pre-cycled at room temperature in 1 M LiNO₃ and 0.5 M Li₂SO₄ electrolytes to 40–50% of the initial capacity were then heated to a higher temperature of 60 °C and additionally cycled another 10 times (Fig. 11). A change in the cell capacity would provide an indication of the kind of resistance in these cells. If the cell resistance was ionic in nature (e.g. due to higher ionic resistance of the surface layer on LCO, Fig. 5), an increase in temperature would increase the capacity of the cells since ionic resistance decreases at higher temperatures. On the other hand, if the resistance growth was mostly electronic (e.g. due to higher electronic resistance of such a layer), higher temperature tests would only result in similar or lower cell capacity because electronic resistance is not significantly impacted by temperature (while higher temperature may, in principle, induce further growth of the surface layer). In our case, we noticed a significant increase in the capacity at higher temperatures. On the other hand, if the resistance growth was mostly electronic (e.g. due to higher electronic resistance of such a layer), higher temperature tests would only result in similar or lower cell capacity because electronic resistance is not significantly impacted by temperature (while higher temperature may, in principle, induce further growth of the surface layer). In our case, we noticed a significant increase in the capacity at higher temperatures, indicating that the cell resistance was mostly ionic in nature. An increase in capacity with temperature was seen in both cells (with 0.5 M Li₂SO₄ and the 1 M LiNO₃ electrolytes). However, cell stability in 0.5 M Li₂SO₄ at 60 °C was noticeably better, consistent with its better stability at room temperature.

Based on the above-described observations of loss of discharge capacity in various concentration aqueous electrolytes (Fig. 2 and 3), correlated rise in impedance (Fig. 3 and 4), and formation of a surface layer (Fig. 5) rich in Co(III)O (Fig. 6–8), below we weigh possible explanations for the loss of discharge capacity and the benefits of higher salt concentrations. Firstly, multiple observations suggest that diminishing discharge capacity predominantly results from the formation and continuous growth of an ionically-resistive layer due to side reactions of LiCoO₂ with aqueous electrolytes. Larger diameter impedance arcs in the Nyquist plots (Fig. 4) (e.g. larger ionic resistances due to surface layer formation) correlate well with more diminished capacity. Increase in polarization with cycle number observed in the voltage profiles (Fig. 3) demonstrate similar trends. A large rise in capacity...
observed in degraded cells after increasing the temperature from ambient temperature to 60 °C suggests that capacity can be largely gained back by overcoming an ionic resistance. A clear correlation between thicker surface layer formation (Fig. 5, TEM and Fig. 6, XPS) in most degraded cells is consistent with the expectation that the thickness of the surface layer should be proportional to the ionic resistance it creates (assuming compositional differences in the surface layer do not hugely impact the resistance for Li+ motion of this surface layer). Increasing salt concentration in aqueous solutions effectively reduces the concentration of water molecules in electrolytes, which are proposed to be mostly responsible for the Co(II)O growth on the LCO surface.

Secondly, dissolution of active material into the electrolyte could also plausibly lead to capacity loss (as in previously studied LFP cathodes4), either directly due to the loss of active material or due to reduced inter-particle electrical connectivity. However, since a significant change in the morphology of particles was not observed via SEM studies of the particles before and after electrochemical cycling, since the electrolyte color did not change after cycling (hexaqua-cobalt(II) ions are pink) and since a significant loss of capacity could be reversed at higher temperatures (Fig. 10), we believe that the significant dissolution of LCO is very unlikely to be a dominant degradation mechanism.

Conclusions

The performance of LCO was systematically investigated in aqueous electrolytes using two low-cost salts of lithium at different salt concentrations. High capacity utilization and rather stable performance was observed in most cells. Higher electrolyte concentration as well as the use of Li2SO4 over LiNO3 favored more stable performance. The use of concentrated Li2SO4 electrolyte allowed us to achieve a remarkable LCO stability with less than 13% degradation after 1500 cycles.

By measuring changes in the cell polarization, conducting EIS studies and increasing temperature of the cells after degradation we identified that the growth of the ionic resistance is the dominant degradation phenomenon. Further studies linked the formation of the layer on the surface of LCO particles to the observed impedance growth. High resolution TEM studies revealed the disordered nature of such a layer. A thicker layer was observed in more degraded cells. Analysis of the O:Co ratio and Co binding energy by XPS studies revealed that this surface layer is composed of ionically resistive Co(II) oxide. Higher degree of conversion of Co(II) ions on the surface to Co(III) ions was found to correlate well with larger impedance growth and more significant cell degradation. Increasing salt concentration in aqueous solutions effectively reduced the concentration of water molecules in electrolytes, which are proposed to be mostly responsible for the CoO growth on the LCO surface. XRD studies suggested that the change in LCO structure and composition was purely a surface phenomenon and that the bulk of the material remained unchanged.

Experimental section

Electrode preparation

Commercial lithium cobalt oxide (99.8%, Sigma Aldrich, USA) was mixed with pure black conductive additive (Superior Graphite, USA) and polyvinylidene difluoride (HSV 900, Kynar, France) binder in the ratio 70 : 15 : 15. This mixture was stirred along with N-methyl pyrrolidone (Sigma-Aldrich, USA) for 24 hours on a magnetic stirrer. The slurry was then cast onto a titanium foil (99.6%, GalliumSource LLC, USA) of 0.0125 mm thickness. These electrodes were dried at 70 °C for 12 hours. Circular electrodes were then cut out from these foils. Working electrodes (WE) of 7/16” ☉ counter electrodes (CE) of 7/8” ☉ were used. The active material layer of the working electrode was also thinner (0.003”) than for counter electrode (0.008”) so that the active mass of the CE was at least 5 times larger than that of the WE.

Electrochemical testing

For charge discharge studies, the WE and CE were spot-welded onto titanium flags (Trinity Brand Industries, USA) and sandwiched between two Teflon blocks using a glass fiber separator (GF/B grade Whatman Glass microfiber). The assembly was immersed in 100 ml of the aqueous electrolyte. The electrolytes were prepared by dissolving either lithium nitrate (99%, Alfa Aesar) or lithium sulfate (98%, Sigma-Aldrich) in 100 ml of distilled water. Different concentrations of electrolytes (1 M, 5 M and 9 M for LiNO3 and 0.5 M, 1 M and 3 M for Li2SO4) were prepared to study the effect of salt concentration on the stability of LCO.

Constant current charge–discharge experiments were performed using a 25% delithiated counter electrode which also served as the reference electrode in the setup (the counter electrode was delithiated separately by 25% of its total capacity by mass, using a constant current and a titanium foil counter electrode). The WE was cycled between +0.15 V to −0.2 V vs. the CE. These tests were conducted using an Arbin Testing System (Arbin Instruments, USA).

For cyclic voltammetry, an Ag/AgCl electrode (3 M NaCl) was used as the reference electrode and a 25% delithiated LCO electrode was used as the counter electrode. CV data was collected at a scan rate of 0.05 mV s−1 using a Gamry Reference 600 Potentiostat.

EIS measurements were also taken after cycling LCO in different electrolytes using the Gamry Potentiostat. The impedance measurements were taken between 10 MHz to 0.05 Hz.

Post cycling electrode characterization

After cycling, the working electrodes were washed with distilled water and dried in ambient temperature. These were then characterized to analyze for changes in structure and composition. SEM images were taken using the LEO 1530 thermally assisted field emission SEM with EDS. A 4 kV accelerating voltage was used for sample imaging. TEM images were collected using the Technai G2 F30 transmission electron microscope operated between 100–300 kV. For XRD, the cycled electrodes were mounted
flat onto the sample holder of a X’Pert Pro Alpha-1 instrument. A Cu Kα source was used at an accelerating voltage of 45 kV and a current of 40 mA. XPS data was collected using a Thermo K-Alpha XPS spectrometer with an Al Kα source. The pass energy was kept at 200 eV for survey scans and 50 eV for detailed scans.

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References