

## MIT Open Access Articles

*A Surface Se#Substituted LiCo[O 2- # Se # ] Cathode with Ultrastable High#Voltage Cycling in Pouch Full#Cells*

The MIT Faculty has made this article openly available. **Please share** how this access benefits you. Your story matters.

**Citation:** Zhu, Zhi, Wang, Hua, Li, Yao, Gao, Rui, Xiao, Xianghui et al. 2020. "A Surface Se# Substituted LiCo[O 2-  $\delta$  Se  $\delta$  ] Cathode with Ultrastable High#Voltage Cycling in Pouch Full# Cells." *Advanced Materials*, 32 (50).

**As Published:** 10.1002/ADMA.202005182

**Publisher:** Wiley

**Persistent URL:** <https://hdl.handle.net/1721.1/138196>

**Version:** Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

**Terms of use:** Creative Commons Attribution-Noncommercial-Share Alike



# A Surface Se-Substituted $\text{LiCo}[\text{O}_{2-\delta}\text{Se}_\delta]$ Cathode with Ultrastable High-Voltage Cycling in Pouch Full-Cells

Z. Zhu, X. Xiao

To be published in "ADVANCED MATERIALS"

November 2020

Photon Sciences

**Brookhaven National Laboratory**

**U.S. Department of Energy**

USDOE Office of Science (SC), Basic Energy Sciences (BES) (SC-22)

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

## **DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

# A Surface Se-Substituted LiCo[O<sub>2-δ</sub>Se<sub>δ</sub>] Cathode with Ultrastable High-Voltage Cycling in Pouch Full-Cells

Zhi Zhu, Hua Wang, Yao Li, Rui Gao, Xianghui Xiao, Qipeng Yu, Chao Wang, Iradwikanari Waluyo, Jiabin Ding, Adrian Hunt, and Ju Li\*

Cycling LiCoO<sub>2</sub> to above 4.5 V for higher capacity is enticing; however, hybrid O anion- and Co cation-redox (HACR) at high voltages facilitates intrinsic O<sup>α-</sup> (α < 2) migration, causing oxygen loss, phase collapse, and electrolyte decomposition that severely degrade the battery cyclability. Hereby, commercial LiCoO<sub>2</sub> particles are operando treated with selenium, a well-known anti-aging element to capture oxygen-radicals in the human body, showing an “anti-aging” effect in high-voltage battery cycling and successfully stopping the escape of oxygen from LiCoO<sub>2</sub> even when the cathode is cycled to 4.62 V. Ab initio calculation and soft X-ray absorption spectroscopy analysis suggest that during deep charging, the precoated Se will initially substitute some mobile O<sup>α-</sup> at the charged LiCoO<sub>2</sub> surface, transplanting the pumped charges from O<sup>α-</sup> and reducing it back to O<sup>2-</sup> to stabilize the oxygen lattice in prolonged cycling. As a result, the material retains 80% and 77% of its capacity after 450 and 550 cycles under 100 mA g<sup>-1</sup> in 4.57 V pouch full-cells matched with a graphite anode and an ultralean electrolyte (2 g Ah<sup>-1</sup>).

As the pioneer cathode for rechargeable Li-ion battery,<sup>[1]</sup> LiCoO<sub>2</sub> (LCO) is still dominating today's battery markets in consumer electronic devices, due to its high volumetric energy density and stable cycling. However, as LCO is only cycled within 4.35 V and 165 mAh g<sup>-1</sup> at the present to meet the industrial-level cycling life,<sup>[2]</sup> there is still a large space to increase its utilizable capacity by charging LCO to higher voltages before it reaches its theoret-

ical capacity of 274 mAh g<sup>-1</sup>.<sup>[3]</sup> Stabilizing high-voltage LCO cycling is a hot topic in both academic and industrial research.<sup>[3,4]</sup> However, the exact mechanism that caused the quick fading of high-voltage LCO has not yet reached consensus.<sup>[5,6]</sup>

The band energy diagram in Figure S1 in the Supporting Information shows that cycling LCO to high voltage must entail a hybrid O anion (O<sup>2-</sup>→O<sup>α-</sup>, α < 2) and Co cation-redox (HACR).<sup>[7,8]</sup> It is tempting to “exploit” HACR in LCO for much higher capacity, e.g., if LCO is charged to above 4.6 V, more than 220 mAh g<sup>-1</sup> can be obtained; however, because of the reduced ionic radius and electrostatic force, the oxidized O<sup>α-</sup> would become much mobile<sup>[9]</sup> and more likely to escape from the particle, resulting in oxygen loss (OL).

Continuous OL can be a killer problem to high-voltage cycling.<sup>[10]</sup> First, OL causes irreversible phase transformations (CoO<sub>2</sub>→Co<sub>3</sub>O<sub>4</sub>)<sup>[11]</sup> (Figure S2, Supporting Information). As Co<sub>3</sub>O<sub>4</sub> is a “bad” spinel with both octahedral and tetrahedral Co occupation that block Li<sup>+</sup> diffusion,<sup>[6]</sup> when the “densified” Co<sub>3</sub>O<sub>4</sub> grows thick enough to enclose all the LCO lattices, the percolating Li<sup>+</sup> diffusion can be terminated, causing dramatic impedance increase. Second, as widely reported,<sup>[12,13,14]</sup> the oxygen released from the cathode, including O<sub>2</sub> and O<sup>α-</sup> radicals, is highly oxidative, which could decompose the carbonate-electrolyte quickly and produce a thick cathode-electrolyte interface (CEI) that degrades battery cycling.

Therefore enabling HACR but preventing OL is the key to developing a stable high-voltage LCO cathode, and decreasing oxygen mobility at the particle surface should be the first priority. Though the use of foreign coatings was attempted in previous research,<sup>[15]</sup> few addressed the fundamental issue regarding the HACR-induced OL at high voltages, so they rarely achieved industrial-level LCO cycling at above 4.5 V, especially in graphite-anode matched full-cells. Hereby, in order to shut down OL at high voltages, we precoated commercial LCO (C-LCO) crystals with selenium (Se). As we will discuss later in this work, during high-voltage charging, the precoated Se would not only soak up the OL from the cathode to prevent it from attacking the electrolyte, but also substitute the

oxidized O<sup>α-</sup> at the charged particle surface (Li<sub>1-x</sub>CoO<sub>2</sub><sup>α-</sup> +  $\frac{3\delta}{2}$  Se→Li<sub>1-x</sub>Co[O<sub>2-δ</sub>Se<sub>δ</sub><sup>β+</sup>] +  $\frac{\delta}{2}$  SeO<sub>2</sub>) to eliminate oxygen vacancies

Dr. Z. Zhu, Dr. H. Wang, Dr. Y. Li, Dr. R. Gao, Dr. Q. Yu, Dr. C. Wang, Prof. J. Li

Department of Nuclear Science and Engineering and Department of Materials Science and Engineering  
Massachusetts Institute of Technology  
Cambridge, MA 02139, USA  
E-mail: liju@mit.edu

Dr. Y. Li

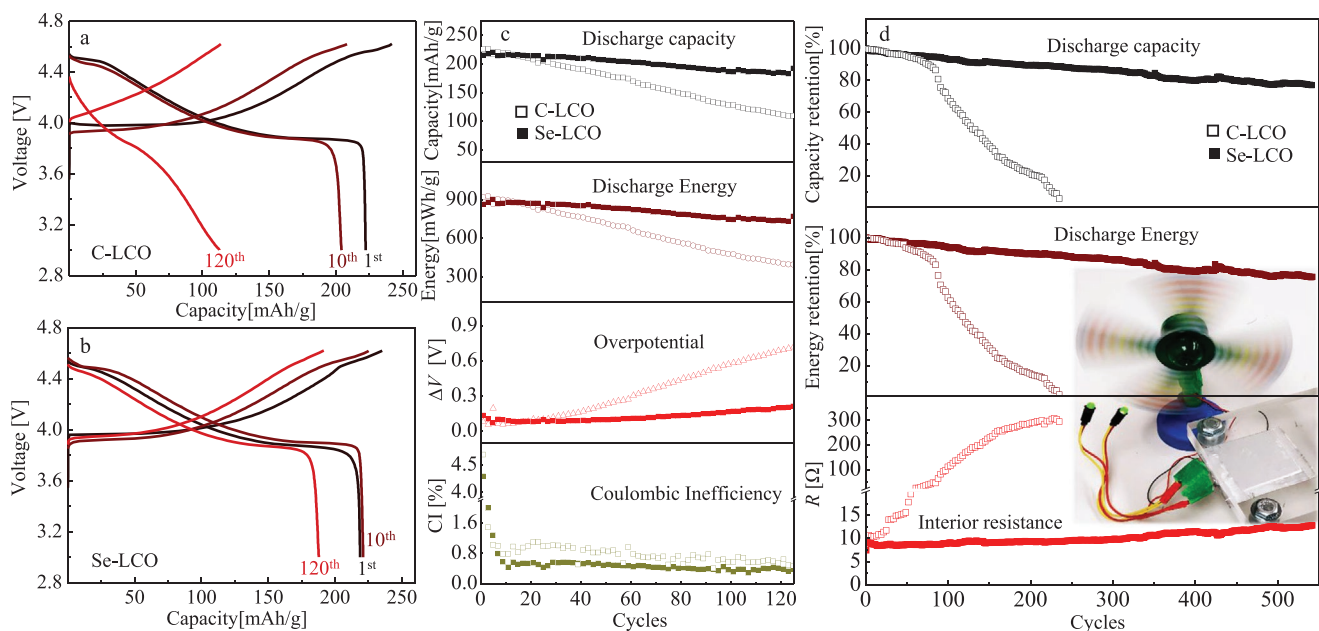
State Key Lab of Metal Matrix Composites  
Shanghai Jiao Tong University  
Shanghai 200240, China

Dr. X. Xiao, Dr. I. Waluyo, Dr. A. Hunt  
National Synchrotron Light Source II  
Brookhaven National Laboratory  
Upton, NY 11973, USA

Dr. J. Ding

Instrumental Analysis Center  
Shanghai Jiao Tong University  
Shanghai 200240, China

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.202005182>.



**Figure 1.** The electrochemical performances of C-LCO and Se-LCO cathodes in coin half-cells and pouch full-cells. a,b) The charge/discharge profiles of C-LCO (a) and Se-LCO cathode (b) within 3.0–4.62 V in coin half-cells under  $70 \text{ mA g}^{-1}$ . c) The cycling of discharge capacities, energy densities, overpotentials, and Coulombic inefficiencies of C-LCO and Se-LCO cathodes within 3.0–4.62 V in coin half-cells under  $70 \text{ mA g}^{-1}$ . d) The cycling retention of discharge capacities, energy densities, and interior resistance of C-LCO and Se-LCO pouch full-cells with graphite anodes under  $100 \text{ mA g}^{-1}$  to 4.57 V followed with floating current of  $40 \text{ mA h g}^{-1}$  again to 4.57 V and discharge to 2.95 V under  $100 \text{ mA g}^{-1}$ .

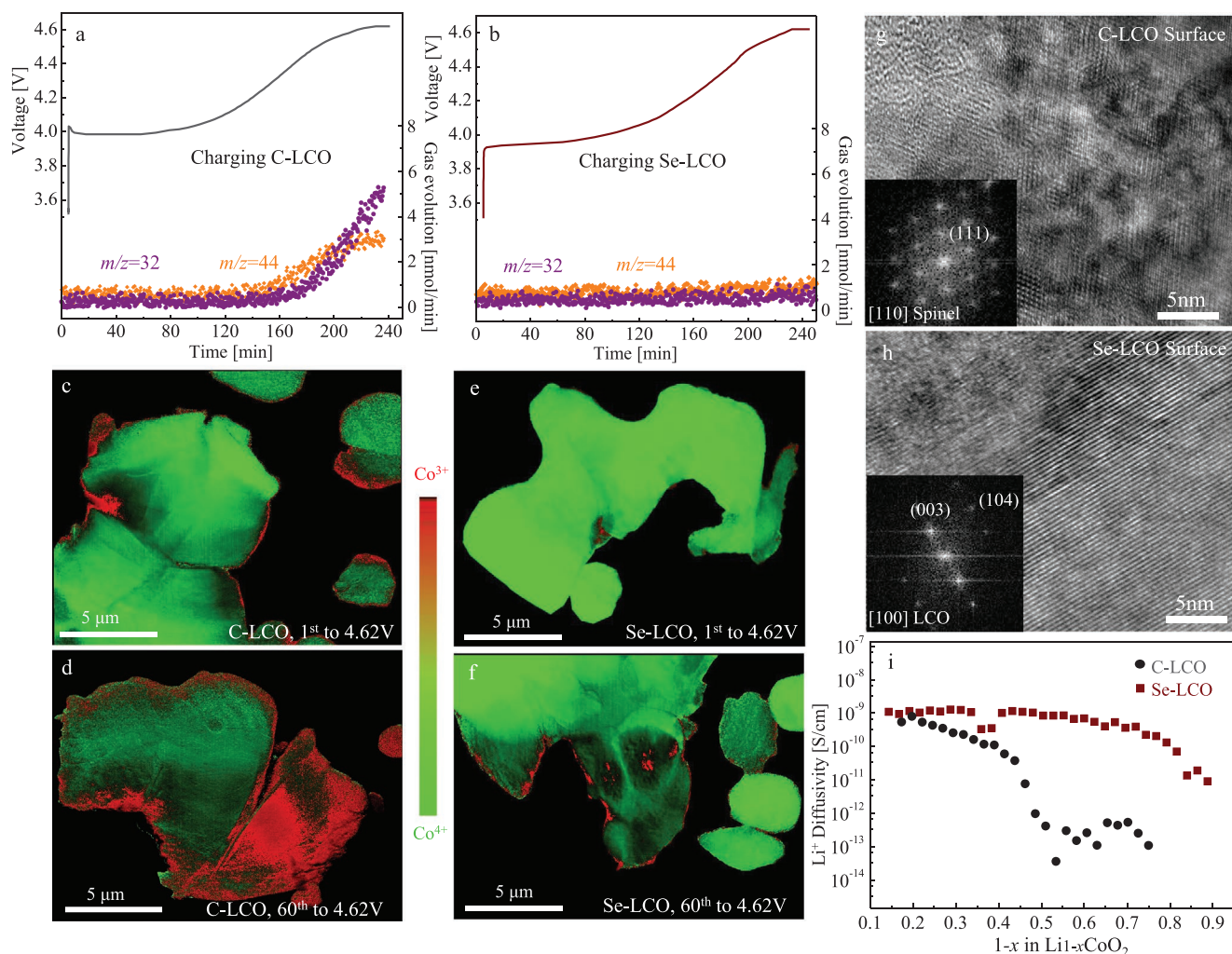
and replenish electrons ( $\text{Se} \rightarrow \text{Se}^{\beta+}$ ) to the charged  $\text{O}^{\alpha-}$  ions ( $\text{O}^{\alpha-} \rightarrow \text{O}^{2-}$ ), reducing the mobile  $\text{O}^{\alpha-}$  ions back to immobile  $\text{O}^{2-}$  at the charged particle surface, to shut down the global oxygen migration in the prolonged cycling. Se is a soft metalloid and an important antiaging element in biology<sup>[16]</sup> in the form of selenocysteine  $-\text{CH}_2-\text{SeH}$  that captures the oxygen-radical species in the human body.<sup>[17]</sup> In this study, we will show that Se would also have an “antiaging” effect on the high-voltage LCO battery cycling by eliminating OL from the cathode.

In this work, we demonstrated that the surface Se-substituted LCO (Se-LCO) has greatly suppressed OL and phase collapse during high-voltage cycling. Moreover, the Se-LCO cathode also mitigated electrolyte decomposition, CEI growth, and acidic corrosion (e.g., hydrofluoric acid (HF)) to stabilize the interface kinetics. Therefore, Se-LCO displayed greatly stabilized cycling even when it was charged to 4.62 V and exhibited ultrastable high-voltage cycling in full-cells that matched with graphite anode and ultralean electrolyte ( $2 \text{ g Ah}^{-1}$ ). Finally, ab initio calculation and soft X-ray absorption spectroscopy (sXAS) analysis were also conducted to understand the mechanism of  $\text{Se}^{\beta+}$  substitution at the oxygen anion site and the stabilization of OL during high-voltage cycling.

The C-LCO and Se-LCO electrodes were first tested in coin half-cells within 3–4.62 V, and the charge/discharge profiles in **Figure 1a,b** showed that in the 1st cycle, C-LCO was charged to  $242 \text{ mAh g}^{-1}$  and discharged to  $223 \text{ mAh g}^{-1}$  under  $70 \text{ mA g}^{-1}$ , and Se-LCO was charged to  $235 \text{ mAh g}^{-1}$ , discharged to  $218 \text{ mAh g}^{-1}$ . Though Se-LCO had slightly decreased initial capacity due to the coated Se, after 120 cycles, the voltage profile of C-LCO severely deformed, indicating a devastating high-voltage cycling degradation, but while that of Se-LCO remained very stable.

Figure 1c shows the cycling performance of C-LCO and Se-LCO within 3.0–4.62 V in half-cells under  $70 \text{ mA g}^{-1}$ . Se-LCO retained  $189 \text{ mAh g}^{-1}$  and  $746 \text{ mWh g}^{-1}$  after 120 cycles, whereas those of C-LCO decreased to  $111 \text{ mAh g}^{-1}$  and  $402 \text{ mWh g}^{-1}$ . More crucially, the overpotential ( $\Delta U \equiv U_{\text{ch}} - U_{\text{disch}}$ , where  $U_{\text{ch}}$  and  $U_{\text{disch}}$  are the average charge and discharge potential vs  $\text{Li}^+/\text{Li}$ ) of Se-LCO ( $\Delta U_{\text{Se-LCO}}$ ) only increased by 170 mV after 120 cycles. However,  $\Delta U_{\text{C-LCO}}$  increased by 620 mV after 120 cycles, almost four times that of  $\Delta U_{\text{Se-LCO}}$ . The irreversible capacity in each cycle was investigated by comparing the cyclic Coulombic inefficiency (CI  $\equiv 100\% - \text{CE}$ , where CE means Coulombic efficiency) in **Figure 1c**. The average  $\text{CI}_{\text{Se-LCO}}$  was less than half of  $\text{CI}_{\text{C-LCO}}$  in cycling, thus the side reactions in the Se-LCO cycling were suppressed by at least 50% in each cycle, including that from electrolyte decomposition and chemical corrosion from the side products (e.g., HF) in the electrolyte.

The C-LCO and Se-LCO cathodes were then cycled in pouch full-cells matched with graphite anodes and ultralean electrolyte ( $2 \text{ g Ah}^{-1}$ ) within 2.95–4.57 V under  $100 \text{ mA g}^{-1}$ . The full-cell cycling in **Figure 1d** showed that while the capacity and energy density of C-LCO rapidly faded to below 50% within 100 cycles and totally “died” within 250 cycles, Se-LCO stably retained 80% of its capacity (79% of energy-density) after 450 cycles and 77% of its capacity (75% of energy-density) after 550 cycles. The much poorer cycling stability of C-LCO in full-cells (**Figure 1d**) compared to in half-cells (**Figure 1c**) can be understood from the quick depletion of the lean electrolyte. In contrast, because the prevented OL from Se-LCO can help mitigate the electrolyte consumption, and moreover the carbonate-electrolyte (with  $\text{LiPF}_6$  salt) has better compatibility with the graphite anode,<sup>[18]</sup> Se-LCO had even displayed much more stable high-voltage cycling in the full-cell (**Figure 1d**) than in the



**Figure 2.** Tracking of oxygen release and Co reduction, and the phases and Li<sup>+</sup> diffusivities in the cathodes. a, b) DEMS during charging the C-LCO cathode (a) and the Se-LCO cathode (b) to 4.62 V. c–f) The Co valence mapping in the C-LCO (c, d) and Se-LCO (e, f) particles when charged to 4.62 V in the 1st (c, e) and 60th (d, f) cycles. The color scheme indicates the Co valence change from +3 (in red) to +4 (in green). g, h) The HRTEM images of the C-LCO (g) and Se-LCO (h) particles near the surface after 120 cycles and FIB preparation; insets are the FFT pattern from the HRTEM images. i) The Li<sup>+</sup> diffusivity within the C-LCO and Se-LCO cathodes in the 120th cycle.

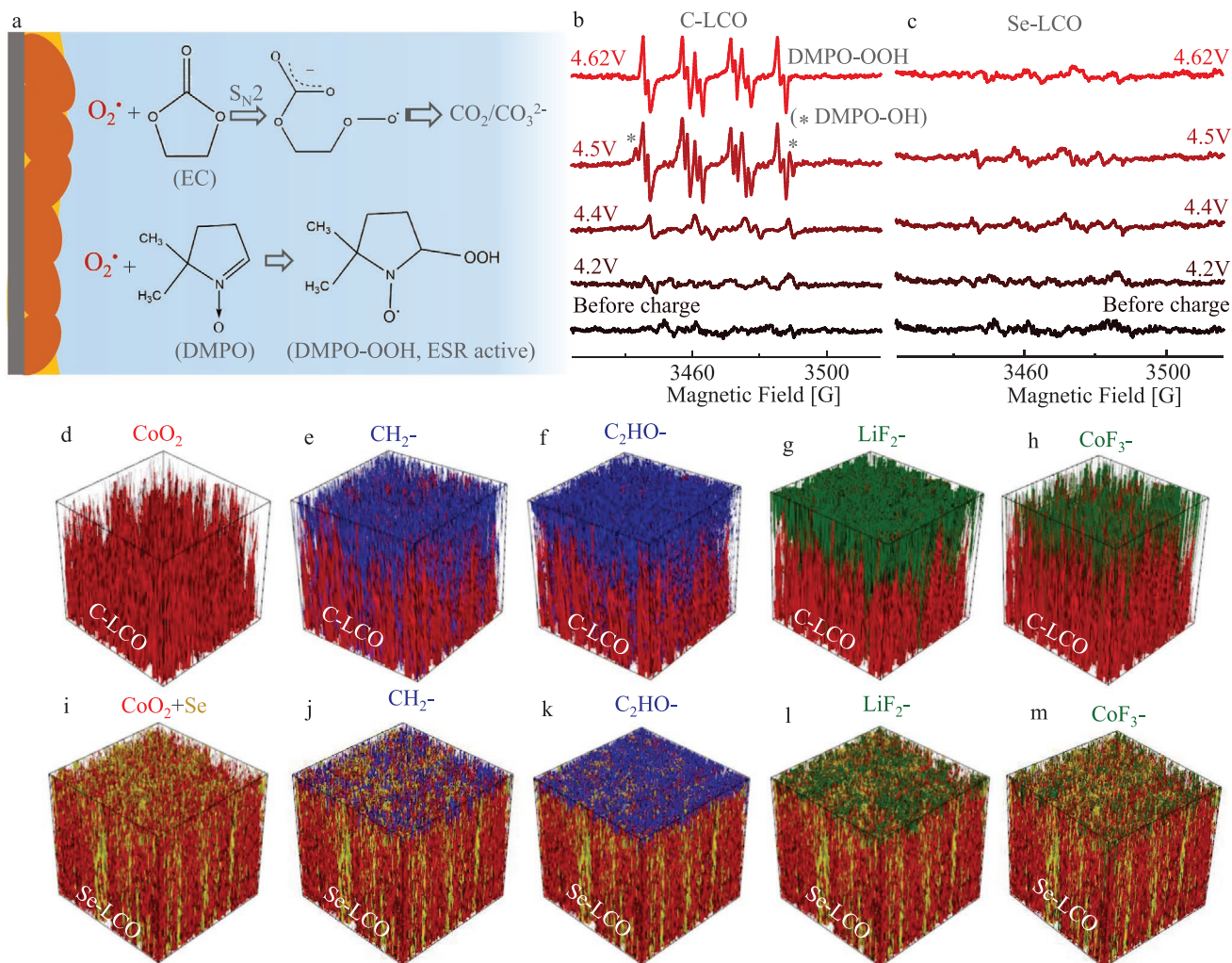
half-cell (Figure 1c). This is the first time that one reported such ultrastable cycling of a prototype 4.57 V LCO pouch full-cell, so we believe this work could be a significant milestone for developing an industrial-scale high-voltage LCO battery.

Additionally, the interior resistance ( $R$ ) of the full-cell was calculated by  $R \equiv V/2i$ , where  $i$  is the cycling current, and is shown in Figure 1d. Though C-LCO and Se-LCO had similar initial  $R$  of  $\approx 12 \Omega$ , while  $R_{\text{C-LCO}}$  increased by  $\approx 300 \Omega$  after 250 cycles,  $R_{\text{Se-LCO}}$  only increased by  $\approx 5 \Omega$  after 550 cycles, so that the average  $R$  increase of Se-LCO ( $\Delta R_{\text{Se-LCO}}$ ) in each cycle was less than 1/100 of  $\Delta R_{\text{C-LCO}}$ . The stabilized  $R$  of the Se-LCO full-cell had not only maintained the applicable energy density in cycling, but would also decrease the heat generation in a practical battery pack and thus favor battery safety under high rates.

We carried out differential electrochemical mass spectroscopy (DEMS) to monitor the O<sub>2</sub> evolution during charging. As shown in Figure 2a, when C-LCO was charged to above 4.5 V, obvious O<sub>2</sub> and CO<sub>2</sub> gas began to release, confirming OL from

C-LCO and the accompanying electrolyte decomposition during the high-voltage charging. However, remarkably, neither O<sub>2</sub> nor CO<sub>2</sub> evolution was detected when Se-LCO was charged to 4.62 V (Figure 2b). The DEMS results demonstrated that the oxygen-migration-induced OL and electrolyte decomposition were greatly suppressed while Se-LCO was charged to high voltage.

O<sub>2</sub> escape from the LCO particle must result in Co reduction,<sup>[9]</sup> where the reduced Co ions (Co<sup>2+/3+</sup>) would migrate to the adjacent tetrahedral or octahedral sites, transforming the charged layered lattice to spinel (Co<sub>3</sub>O<sub>4</sub>) phase.<sup>[11]</sup> This “bad” spinel is not only electrochemically inactive, but also blocks Li<sup>+</sup> diffusion in cycling.<sup>[6]</sup> In this work, we performed Co X-ray absorption near edge structure (XANES) mapping at the National Synchrotron Light Source II (NSLS-II) of Brookhaven National Laboratory, to track the Co valence distribution in the charged particles. As shown in Figure 2c, d, when first charged to 4.62 V, while most of the Co in C-LCO was charged to  $\approx +4$  valence (in green), there appeared a few patches comprising of



**Figure 3.** The prevented generation of oxygen radicals in the electrolyte and 3D cathode surface reconstruction. a) The schematic of the decomposition of the carbonate electrolyte that resulted from the production and release of oxidative oxygen radicals at high voltages. b,c) The EPR signals from the electrolytes with  $10 \times 10^{-3}$  M DMPO added when charging C-LCO (b) and Se-LCO (c) to different voltages. d-m) The 3D reconstruction of  $\text{CoO}_2^-$ ,  $\text{CH}_2^-$ ,  $\text{C}_2\text{HO}^-$ ,  $\text{LiF}_2^-$ , and  $\text{CoF}_3^-$  fragment at the C-LCO (d-h) and Se-LCO (i-m) cathode surface after 120 cycles.

low-valent Co ions ( $\approx +3$ , in red) at the surface, and more seriously, the charged C-LCO particle was almost fully covered by reduced Co ions after 60 cycles. However, very differently, there was very little reduced Co ions in the charged Se-LCO particle in either the 1st or 60th cycle (Figure 2e,f). The Co XANES mapping further confirmed that OL was prevented when Se-LCO was charged to a high voltage.

The suppressed OL and Co reduction, even at high voltage, could help stabilize the particle phase during the Se-LCO cycling. The scanning electron microscopy (SEM) images in Figure S3 in the Supporting Information show that while there were severe cracks and denudation shreds at the C-LCO particle surface after 120 cycles, the morphology of the Se-LCO particle remained very dense and smooth. The high-resolution transmission electron microscopy (HRTEM) images in Figure 2g,h additionally indicated that there were random spinel domains near the C-LCO particle surface, but very differently, the Se-LCO particle still has stable ordered layered lattices. The stabilized layered phase in Se-LCO can greatly maintain the bulk  $\text{Li}^+$  diffusion and interior

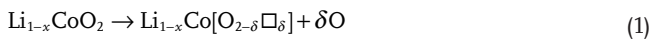
resistance ( $R$ ) in the battery cycling (Figure 1d). The galvanostatic intermittent titration technique (GITT) in Figure S4 in the Supporting Information shows that the voltage drops in titrating Se-LCO were greatly suppressed compared to that of C-LCO in the 120th cycle. The calculated  $\text{Li}^+$  diffusivities ( $D_{\text{Li}^+}$ ) in the 120th discharge (Figure 2i) indicated that the average  $D_{\text{Li}^+}$  of Se-LCO was  $\approx 10^{-9}$   $\text{S cm}^{-1}$ , about 3 orders magnitude higher than that of C-LCO. The high  $D_{\text{Li}^+}$  of Se-LCO significantly maintained the kinetics and stabilized the cell cycling, as shown in Figure 1c,d.

As widely reported,<sup>[13,20]</sup> electrolyte decomposition can be especially aggravated when oxygen radicals<sup>[13,21]</sup> were produced in the electrolyte (e.g., hydroxyl  $\text{HO}\cdot$  or superoxide  $\text{O}_2\cdot^-$ ), which can oxidize the carbonate-solvent with  $\text{S}_{\text{N}}2$  attack<sup>[14]</sup> (Figure 3a). Electron paramagnetic resonance (EPR) spectroscopy was carried out to check the generation of oxygen radicals during charging. For higher experimental accuracy, 5,5-dimethyl-1-pyrroline  $N$ -oxide (DMPO) was added into the electrolyte as a radical trapper to extend these oxygen radicals' lives<sup>[22]</sup> (Figure 3a). Figure 3b,c clearly shows that the electrolyte became EPR active

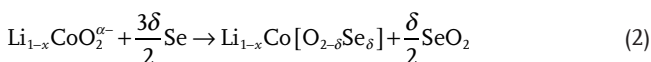
when C-LCO was charged to above 4.4 V. Note that the resonance curve after 4.5 V gradually built a typical six-pairs EPR signal attributed to a classical DMPO–OOH adduct, mixed with a small amount of DMPO–OH,<sup>[23]</sup> so the EPR analysis clearly suggested the generation of O<sub>2</sub>• (with HO•) in the electrolyte when C-LCO was charged to above 4.5 V. However, the EPR response from the electrolyte when Se-LCO was charged to 4.62 V was very low and did not suggest the presence of EPR-active DMPO adducts, so we can infer that the production of oxidative oxygen radicals had been suppressed in the electrolyte when Se-LCO was charged to a high voltage.

The absence of the generation of O<sub>2</sub> from the Se-LCO cathode and oxygen-radicals in the electrolyte would greatly suppress CEI growth the cathode. We then performed time-of-flight secondary-ion mass spectrometry (TOF-SIMS) to analyze the cathode surface after 120 cycles (Figures S5–S7, Supporting Information) and conducted a 3D surface reconstruction. First, it can be seen that the C-LCO crystal was seriously corroded as the surface became very rough (Figure 3d), but the Se-LCO particle remained very smooth (Figure 3i), consistent with the SEM morphology in Figure S3 in the Supporting Information. Then, we used CH<sub>2</sub><sup>–</sup> (Figure 3e,j) and C<sub>2</sub>HO<sup>–</sup> (Figure 3f,k) fragments to represent the CEI component in the 3D reconstruction.<sup>[6]</sup> The much thinner CEI layer covering on the cycled Se-LCO cathode than on the cycled C-LCO (Figure S7, Supporting Information) demonstrated that while the carbonate-solvent was severely decomposed in the C-LCO cycling, it remained stable in the Se-LCO cycling. Additionally, the Se-LCO surface also prevented acidic corrosion from the side-products (e.g., HF) in the electrolyte, as the LiF<sub>2</sub><sup>–</sup> (Figure 3l) and CoF<sub>3</sub><sup>–</sup> (Figure 3m) layers at the Se-LCO cathode surface were much thinner than those at the C-LCO surface (Figure 3g,h) after 120 cycles. The much-thinner CEI layer at the Se-LCO particle surface, containing less fluoride, would greatly favor the interfacial Li<sup>+</sup> transfer. The EIS analysis in Figure S8 in the Supporting Information clearly indicates that the interface impedance of Se-LCO was less than 1/2 that of C-LCO (≈150 Ω) after 120 cycles. Additionally, the Co deposition at the graphite anode in the Se-LCO matched full-cell was also suppressed, compared to that cycled with C-LCO (Figure S9 and Table S1, Supporting Information), which also favored the full-cell cycling, as shown in Figure 1d.

In order to understand how the coated Se prevented OL from LCO during high-voltage cycling, we first conducted an ab initio calculation to predict the possible behaviors between the deeply charged Li<sub>1-x</sub>CoO<sub>2</sub> lattice and Se. According to the first-principles density functional theory (DFT) relaxation calculation in Figure S10 in the Supporting Information, when the mobile oxidized O<sup>α-</sup> initially leaves the deeply charged lattice (Figure 4a)



the Se substitution on these leftover oxygen vacancy (Vo) sites in the charged lattice would be favored (Figure 4b). That is, an exchange strategy of O<sup>α-</sup>↔Se would be more preferable than leaving Vo in the deeply charged LCO lattice that occurred in C-LCO at high voltage, by following an operando reaction of



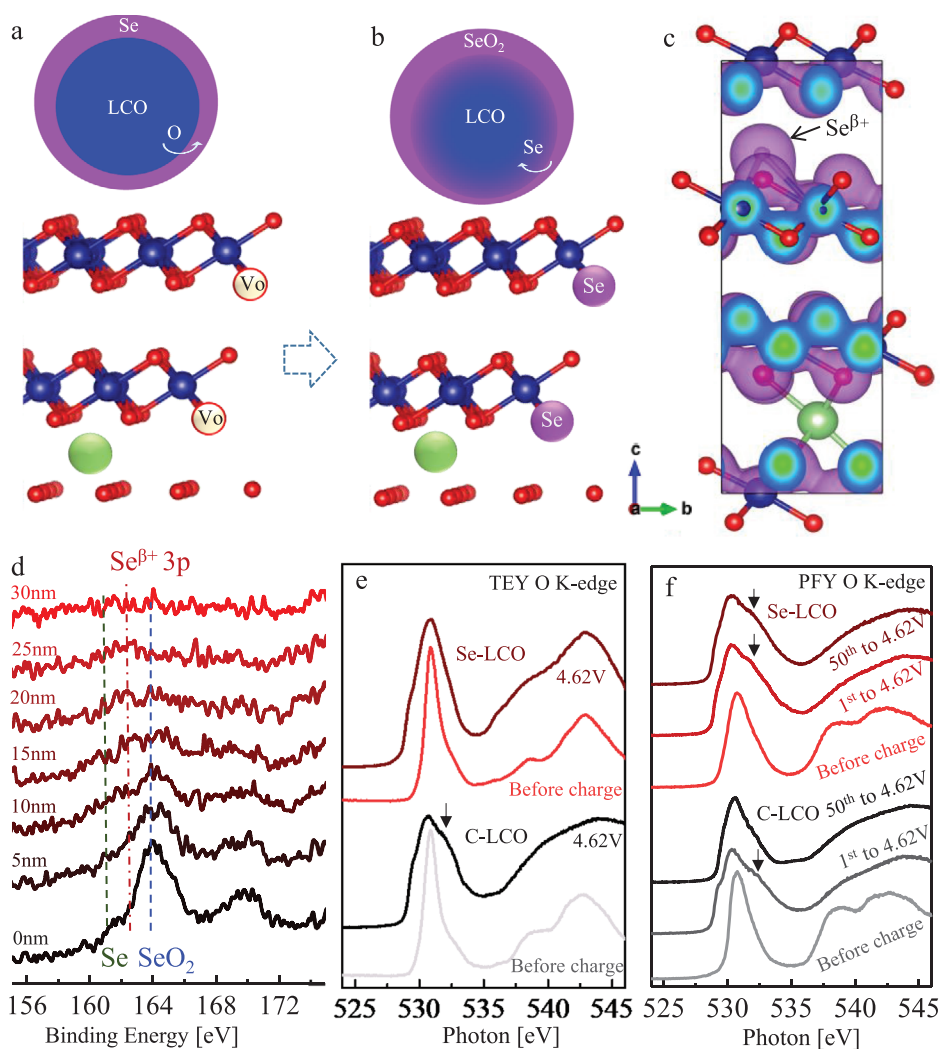
then we can get a Se-substituted lattice near the charged Se-LCO particle surface (Figure 4a,b).

In this process, the coated Se would first catch the initial escaping oxygen by forming a SeO<sub>2</sub> outer-layer to prohibit the escaping oxygen from reacting with the precious electrolyte. This process can be experimentally verified by the XPS analysis in Figure S11 in the Supporting Information, which showed that the precoated metallic Se was gradually oxidized to SeO<sub>2</sub> in the initial 10 cycles.<sup>[24]</sup> More crucially, the charge density distribution from first-principles DFT calculation, shown in Figure 4c, indicated electron transfer from Se atom to Co atom, where the Bader charge analysis in Table S2 in the Supporting Information also verified that the Se ions in the Se-substituted lattice has positive valence (Li<sub>1-x</sub>Co[O<sub>2-δ</sub>Se<sup>β+</sup>]). The positive Se<sup>β+</sup> in the lattice was also confirmed by the XPS depth analysis in Figure 4d, where the new Se 3p peak at ≈162.3 eV between the metallic Se (161 eV) and SeO<sub>2</sub> (164 eV) that appeared beneath the SeO<sub>2</sub> outer-layer suggested an average Se valence of 0 < β < 4.<sup>[25]</sup>

DFT calculations by Lee and Persson showed that the potential energy barrier of O<sup>1-</sup>–V<sub>O</sub> exchange was 0.9 eV, while that of O<sup>2-</sup>–V<sub>O</sub> exchange was 2.3–4.0 eV.<sup>[9]</sup> Thus at room temperature (k<sub>B</sub>T = 0.025 eV), oxygen migration is practically possible only if a) α < 2, and b) there is a V<sub>O</sub> adjacent to O<sup>α-</sup>. The role of Se in stopping the ill effects of reaction (1) can be threefold: i) the formation of SeO<sub>2</sub>, a 1D solid polymer oxide, prevents the escaping oxygen from attacking the precious electrolyte; ii) additional Se “plugs” into the V<sub>O</sub> sites inside the lattice near the surface, thus reducing oxygen mobility by removing one necessary condition for O<sup>α-</sup>–V<sub>O</sub> exchange; otherwise, such V<sub>O</sub> will be pumped back toward the interior of the ≈10 μm LCO crystal to further facilitate oxygen migration in the interior to cause continuous OL; iii) Se-substitution can transplant the pumped charges from the oxidized O<sup>α-</sup>, by replenishing electrons to the oxidized O<sup>α-</sup> (Se–Co→O) and reducing the mobile oxidized O<sup>α-</sup> ions back to immobile O<sup>2-</sup> ions, so the other necessary condition for O<sup>α-</sup>–V<sub>O</sub> exchange is also removed. This is accomplished by the “sacrificial” oxidation of Se (Se→Se<sup>β+</sup>) in Li<sub>1-x</sub>Co[O<sub>2-δ</sub>Se<sup>β+</sup>], as verified with both DFT calculation and XPS analysis. For such “sacrificial” oxidation of Se to happen, the equilibrium potential of U<sup>eq</sup>(Se<sup>β+/0</sup>) should be somewhat lower than U<sup>eq</sup>(O<sup>α-/2-</sup>), so instead of oxygen anion-oxidation near the surface, Se is sacrificially oxidized at the high voltages, especially when there is V<sub>O</sub> in the lattice. Additionally, the DFT calculation showed that while the substituted Se<sup>β+</sup> sat near the vacated V<sub>O</sub> site, it was not at the V<sub>O</sub> site exactly but was significantly elevated toward the adjacent Li layer (LiL) (Figure 4c; Figure S10, Supporting Information), and moreover, the migration energy barriers of Se<sup>β+</sup> in LiL was surprisingly small (<0.35 eV; Figure S12, Supporting Information). Thus, the highly charged LCO lattice also provides fluent kinetic pathways for the operando inward diffusion of Se<sup>β+</sup> to prevent oxygen migration.

From a crystal chemistry point of view, cation substitution of anion site would be quite unusual. However, as Figure 4c shows, Se<sup>β+</sup> was not at the V<sub>O</sub> site exactly and was significantly elevated out of the anion plane. So we believe a more acceptable interpretation would be the formation of “selenite (SeO<sub>3</sub><sup>2-</sup>) like” resonant structures where Se would take the formal charge of β = 4+ if oxygen is taken to be 2–, or lower-valence (0 < β < 4) analogs. So a way of looking at the LCO surface passivation





**Figure 4.** The Se-substitution and prevention of oxygen migration in the highly charged Se-LCO particle. a) The schematic and lattice structure when the mobile O escapes from the charged LCO lattice with leftover  $V_O$ . b) The schematic and lattice structure when Se substitutes  $V_O$ . c) The charge density distribution in the charged Se-LCO lattice from first-principles DFT calculation. d) The XPS Se 3p edge at different depths in the Se-LCO particle after 10 cycles, where the green, blue, and red dashed lines indicate the 3p location of metallic Se,  $SeO_2$ , and  $Se^{\beta+}$ . e, f) sXAS O K-edge spectra of C-LCO and Se-LCO under TEY mode (e) and PFY mode (f) at different states of charge.

by Se is the formation of “lithium cobalt selenite” like motifs near the surface, covered by  $SeO_2$  on the outside. This “fixes” the HACR-induced OL, plugs the  $V_O$  and immobilizes oxygen near the surface, thus preventing further OL and  $V_O$  pumping backward into the interior, which eventually would lead to phase collapse into densified “bad spinel”  $Co_3O_4$ .<sup>[26]</sup>

sXAS was performed under TEY mode to investigate the oxidation states of oxygen ions at the charged particle surface.<sup>[27]</sup> In Figure 4e when charged to 4.62 V, while the peak intensity at  $\approx 530$  eV for C-LCO obviously decreased with a new peak appearance at +2 eV higher energy, confirming an expected  $O^{2-} \rightarrow O^{\alpha-}$  reaction at the C-LCO particle surface,<sup>[8]</sup> the TEY sXAS O K-edge of Se-LCO changed very little, verifying that the oxygen ions indeed remained at -2 valence at the charged Se-LCO particle surface. The eliminated  $O^{2-} \rightarrow O^{\alpha-}$  at the Se-LCO particle surface would greatly suppress the global oxygen migration and OL at high voltage,<sup>[10,28]</sup> because even though the oxygen ions

in the particle bulk can still be oxidized, it was enclosed in the bulk and cannot trespass the  $O^{\alpha-}$ -free  $Li_{1-x}Co[O_{2-\delta}Se_{\delta}]$  surface. Furthermore, there is no superabundant  $V_O$  to assist the global oxygen migration (as is well known, surfaces and grain boundaries are typical sources for lattice vacancies, and there are few grain boundaries in these large commercial LCO single crystals), then the bulk HACR ( $O^{2-} \rightarrow O^{\alpha-}$ ) reversibility can be significantly improved in the prolonged Se-LCO cycling. The PFY sXAS O K-edge of C-LCO and Se-LCO in Figure 4f indicated that while both C-LCO and Se-LCO entailed heavy bulk oxygen anion-redox ( $O^{2-} \rightarrow O^{\alpha-}$ ) in the 1st charging,<sup>[27]</sup> only the PFY O K-edge of Se-LCO kept unchanged after 50 cycles, as that of C-LCO showed little fingerprint of oxidized  $O^{\alpha-}$  in the 50th charging.

In summary, in this work commercial LCO material was investigated when it was cycled up to 4.62 V, which showed that the percolating oxygen migration out of the particle at high

voltage caused irreversible phase transformation and aggravated electrolyte decomposition, leading to rapid high-voltage cycling decay. Then, these LCO crystals were coated with Se, and during deep charging, Se did not only catch the escaped oxygen from the cathode to prevent it from attacking the electrolyte, but it would also substitute part of the mobile  $O^{\alpha-}$  in the charged lattice to eliminate  $V_O$ , and transplant the pumped charges  $(2-\alpha)^+$  from the oxidized  $O^{\alpha-}$ , reducing the mobile  $O^{\alpha-}$  ions back to immobile  $O^{2-}$  ions, to stop the further oxygen migration. Therefore, HACR-induced OL phase collapse, and electrolyte decomposition were significantly suppressed in the prolonged cycles to promote an ultrastable high-voltage Se-LCO cycling to the unprecedented 4.57 V in pouch full-cells with graphite anode and ultralean electrolyte ( $2 \text{ g Ah}^{-1}$ ), with 77% capacity retention after 550 cycles under  $100 \text{ mA g}^{-1}$ . The antiaging mechanisms of such Se modification is generic and should be applicable to other layered cathode materials such as Ni-rich and Li-rich NMC materials that involved oxygen anion-redox at high voltage to prevent OL induced issues and stabilize high-voltage and high energy density cycling.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

The authors acknowledge the support from the Watt Energy Technology Lab gift fund. This research used resources of the 18-ID (FXI) and 23-ID-2 (IOS) beamlines of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704. This work was performed in part at the Center for Nanoscale Systems (CNS), a member of the National Nanotechnology Coordinated Infrastructure Network (NNCI), which is supported by the National Science Foundation under NSF award no. 1541959.

## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

cathode materials, global oxygen migration, high-voltage cycling, hybrid redox, Li-ion batteries, lithium cobalt oxides

- [1] K. Mizushima, P. C. Jones, P. J. Wiseman, J. B. Goodenough, *Solid State Ionics* **1981**, 3–4, 171.  
 [2] S. Kalluri, M. Yoon, M. Jo, S. Park, S. Myeong, J. Kim, S. X. Dou, Z. P. Guo, J. Cho, *Adv. Energy Mater.* **2017**, 7, 1601507.

- [3] Q. Liu, X. Su, D. Lei, Y. Qin, J. G. Wen, F. M. Guo, Y. M. A. Wu, Y. C. Rong, R. H. Kou, X. H. Xiao, F. Aguesse, J. Bareno, Y. Ren, W. Q. Lu, Y. X. Li, *Nat. Energy* **2018**, 3, 936.  
 [4] a) J. N. Zhang, Q. H. Li, C. Y. Ouyang, X. Q. Yu, M. Y. Ge, X. J. Huang, E. Y. Hu, C. Ma, S. F. Li, R. J. Xiao, W. L. Yang, Y. Chu, Y. J. Liu, H. G. Yu, X. Q. Yang, X. J. Huang, L. Q. Chen, H. Li, *Nat. Energy* **2019**, 4, 594; b) J. W. Qian, L. Liu, J. X. Yang, S. Y. Li, X. Wang, H. L. L. Zhuang, Y. Y. Lu, *Nat. Commun.* **2018**, 9, 4918.  
 [5] a) A. Van der Ven, M. K. Aydinol, G. Ceder, G. Kresse, J. Hafner, *Phys. Rev. B* **1998**, 58, 2975; b) H. Xia, L. Lu, Y. S. Meng, G. Ceder, *J. Electrochem. Soc.* **2007**, 154, A337; c) M. D. Radin, S. Hy, M. Sina, C. C. Fang, H. D. Liu, J. Vinkeviciute, M. H. Zhang, M. S. Whittingham, Y. S. Meng, A. Van der Ven, *Adv. Energy Mater.* **2017**, 7, 1602888; d) T. Ohzuku, A. Ueda, *J. Electrochem. Soc.* **1994**, 141, 2972; e) H. Wang, Y. I. Jang, B. Huang, D. R. Sadoway, Y. M. Chiang, *J. Electrochem. Soc.* **1999**, 146, 473.  
 [6] M. Yoon, Y. Dong, Y. Yoo, S. Myeong, J. Hwang, J. Kim, S.-H. Choi, J. Sung, S. J. Kang, J. Li, J. Cho, *Adv. Funct. Mater.* **2019**, 30, 1907903.  
 [7] a) Z. Zhu, A. Kushima, Z. Y. Yin, L. Qi, K. Amine, J. Lu, J. Li, *Nat. Energy* **2016**, 1, 16111; b) Y. Qiao, K. Jiang, H. Deng, H. Zhou, *Nat. Catal.* **2019**, 2, 1035; c) S. Venkatraman, Y. Shin, A. Manthiram, *Electrochem. Solid-State Lett.* **2003**, 6, A9.  
 [8] a) W. S. Yoon, K. B. Kim, M. G. Kim, M. K. Lee, H. J. Shin, J. M. Lee, J. S. Lee, C. H. Yo, *J. Phys. Chem. B* **2002**, 106, 2526; b) W. S. Yoon, K. B. Kim, M. G. Kim, M. K. Lee, H. J. Shin, J. M. Lee, *J. Electrochem. Soc.* **2002**, 149, A1305.  
 [9] a) P. F. Yan, J. M. Zheng, Z. K. Tang, A. Devaraj, G. Y. Chen, K. Amine, J. G. Zhang, L. M. Liu, C. M. Wang, *Nat. Nanotechnol.* **2019**, 14, 602; b) E. Lee, K. A. Persson, *Adv. Energy Mater.* **2014**, 4, 1400498.  
 [10] Z. Zhu, D. Yu, Z. Shi, R. Gao, X. Xiao, I. Waluyo, M. Ge, Y. Dong, W. Xue, G. Xu, *Energy Environ. Sci.* **2020**, 13, 1865.  
 [11] M. Yoon, Y. Dong, Y. Yoo, S. Myeong, J. Hwang, J. Kim, S. H. Choi, J. Sung, S. J. Kang, J. Li, *Adv. Funct. Mater.* **2020**, 30, 1907903.  
 [12] a) X. Zuo, C. Fan, X. Xiao, J. Liu, J. Nan, *J. Power Sources* **2012**, 219, 94; b) S. A. Delp, O. Borodin, M. Olguin, C. G. Eisner, J. L. Allen, T. R. Jow, *Electrochim. Acta* **2016**, 209, 498.  
 [13] N.-S. Choi, J.-G. Han, S.-Y. Ha, I. Park, C.-K. Back, *RSC Adv.* **2015**, 5, 2732.  
 [14] V. S. Bryantsev, M. Blanco, *J. Phys. Chem. Lett.* **2011**, 2, 379.  
 [15] a) L. de Biasi, B. Schwarz, T. Brezesinski, P. Hartmann, J. Janek, H. Ehrenberg, *Adv. Mater.* **2019**, 31, 1900985; b) S. Kalluri, M. Yoon, M. Jo, S. Park, S. Myeong, J. Kim, S. X. Dou, Z. P. Guo, J. Cho, *Adv. Energy Mater.* **2017**, 7, 1601507; c) A. Yano, M. Shikano, A. Ueda, H. Sakaebe, Z. Ogumi, *J. Electrochem. Soc.* **2017**, 164, A6116.  
 [16] Y. Zhang, Y. J. Roh, S. J. Han, I. Park, H. M. Lee, Y. S. Ok, B. C. Lee, S. R. Lee, *Antioxidants* **2020**, 9, 383.  
 [17] H. Steinbrenner, H. Sies, *Biochim. Biophys. Acta, Gen. Subj.* **2009**, 1790, 1478.  
 [18] K. Xu, *Chem. Rev.* **2004**, 104, 4303.  
 [19] S.-M. Bak, Z. Shadike, R. Lin, X. Yu, X.-Q. Yang, *NPG Asia Mater.* **2018**, 10, 563.  
 [20] a) J. Li, C. Ma, M. Chi, C. Liang, N. J. Dudney, *Adv. Energy Mater.* **2015**, 5, 1401408; b) L. Hu, Z. Zhang, K. Amine, *J. Power Sources* **2013**, 236, 175; c) M. Hu, X. Pang, Z. Zhou, *J. Power Sources* **2013**, 237, 229.  
 [21] a) S. A. Freunberger, Y. Chen, Z. Peng, J. M. Griffin, L. J. Hardwick, F. Bardé, P. Novák, P. G. Bruce, *J. Am. Chem. Soc.* **2011**, 133, 8040; b) H. Wang, K. Xie, *Electrochim. Acta* **2012**, 64, 29; c) H. Wang, E. Rus, T. Sakuraba, J. Kikuchi, Y. Kiya, H. D. Abruña, *Anal. Chem.* **2014**, 86, 6197.  
 [22] a) J.-L. Clément, N. Ferré, D. Siri, H. Karoui, A. Rockenbauer, P. Tordo, *J. Org. Chem.* **2005**, 70, 1198; b) R. Cao, E. D. Walter, W. Xu, E. N. Nasybulin, P. Bhattacharya, M. E. Bowden, M. H. Engelhard, J. G. Zhang, *ChemSusChem* **2014**, 7, 2436.

- [23] K. P. Madden, H. Taniguchi, *Free Radical Biol. Med.* **2001**, *30*, 1374.
- [24] a) A. J. Green, S. Dey, Y. Q. An, B. O'Brien, S. O'Mullane, B. Thiel, A. C. Diebold, *J. Vac. Sci. Technol., A* **2016**, *34*, 061403; b) X. Huang, Y. Liu, C. Liu, J. Zhang, O. Noonan, C. Yu, *Chem. Sci.* **2018**, *9*, 5178.
- [25] M. Gui, J. K. Papp, A. S. Colburn, N. D. Meeks, B. Weaver, I. Wilf, D. Bhattacharyya, *J. Membr. Sci.* **2015**, *488*, 79.
- [26] Y. Huang, Y. Dong, S. Li, J. Lee, C. Wang, Z. Zhu, W. Xue, Y. Li, J. Li, *Adv. Energy Mater.* **2020**, <https://doi.org/10.1002/aenm.202000997>.
- [27] R. Qiao, L. A. Wray, J.-H. Kim, N. P. Pieczonka, S. J. Harris, W. Yang, *J. Phys. Chem. C* **2015**, *119*, 27228.
- [28] a) Z. Zhu, D. Yu, Y. Yang, C. Su, Y. Huang, Y. Dong, I. Waluyo, B. Wang, A. Hunt, X. Yao, *Nat. Energy* **2019**, *4*, 1049; b) Z. Zhu, R. Gao, I. Waluyo, Y. Dong, A. Hunt, J. Lee, J. Li, *Adv. Energy Mater.* **2020**, *10*, 2001120.