

# In situ healing of dendrites in a potassium metal battery

# Prateek Hundekar<sup>a</sup>, Swastik Basu<sup>a</sup>, Xiulin Fan<sup>b</sup>, Lu Li<sup>a</sup>, Anthony Yoshimura<sup>c</sup>, Tushar Gupta<sup>a</sup>, Varun Sarbada<sup>d</sup>, Aniruddha Lakhnot<sup>a</sup>, Rishabh Jain<sup>a</sup>, Shankar Narayanan<sup>a</sup>, Yunfeng Shi<sup>d</sup>, Chunsheng Wang<sup>b</sup>, and Nikhil Koratkar<sup>a,d,1</sup>

<sup>a</sup>Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180; <sup>b</sup>Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742; <sup>c</sup>Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, NY 12180; and <sup>d</sup>Department of Material Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180

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The use of potassium (K) metal anodes could result in highperformance K-ion batteries that offer a sustainable and low-cost alternative to lithium (Li)-ion technology. However, formation of dendrites on such K-metal surfaces is inevitable, which prevents their utilization. Here, we report that K dendrites can be healed in situ in a K-metal battery. The healing is triggered by currentcontrolled, self-heating at the electrolyte/dendrite interface, which causes migration of surface atoms away from the dendrite tips, thereby smoothening the dendritic surface. We discover that this process is strikingly more efficient for K as compared to Li metal. We show that the reason for this is the far greater mobility of surface atoms in K relative to Li metal, which enables dendrite healing to take place at an order-of-magnitude lower current density. We demonstrate that the K-metal anode can be coupled with a potassium cobalt oxide cathode to achieve dendrite healing in a practical full-cell device.

potassium-ion battery | dendrite healing | safety

**R**echargeable lithium (Li)-ion batteries (LIBs) have emerged as the preeminent energy storage technology over the past few decades, owing to their high energy density and extraordinary cycling characteristics (1, 2). However, the uneven distribution and scarcity of Li in the earth's crust (~20 ppm) makes relying on LIBs as the sole source of energy storage highly impractical and uneconomical (3). Alkaline metal-ion-based batteries such as sodium (Na)-ion batteries (NIBs) and potassium (K)-ion batteries (KIBs) have garnered extensive attention over the past few years, in the hope that their abundant presence in the earth's crust (~2.36 wt % and ~2.09 wt %, respectively, compared to ~0.0017 wt % of Li) and lower costs would aid large-scale energy storage applications (4, 5). NIBs have been intensively investigated in the past few years, while KIBs are gradually gaining widespread attention (6, 7).

The standard potential for K<sup>+</sup>/K is -2.93 V versus the standard hydrogen electrode (SHE), which is comparable to -3.04 V for Li<sup>+</sup>/Li. Also, K theoretically offers a higher operating voltage than Na, since the standard redox potential for  $Na^+/Na$  is -2.71 V versus SHE. In the commonly used ethylene carbonate/diethyl carbonate (EC/DEC) electrolyte, it was determined that K<sup>+</sup>/K is -0.15 V versus the Li<sup>+</sup>/Li (ref. 7). This low potential provides KIBs a superior position among possible alternatives to replace Li-based batteries. It should also be noted that K unlike Li, does not alloy with aluminum at low potentials (8), enabling the utilization of low-cost aluminum foils as the current collector for the anode. Compared to LIBs and NIBs, another important benefit of KIBs is that the K ion exhibits much weaker Lewis acidity (9, 10) and forms smaller solvated ions than those of Li and Na. This allows for higher ionic conductivity and faster transport of solvated K ions, with prospects of improved high-power performance for KIBs.

A variety of anode and cathode materials for K secondary batteries have been explored. Owing to the larger ionic size and mass of  $K^+$ , only a few cathode materials have been reported for

KIBs. Among these, Prussian Blue and its analogs have been reported to reversibly store K ions in nonaqueous electrolytes, but poor volumetric capacity due to the low density of hexacvanoferrates limits their practical applications (8, 11, 12). Recently, Deng et al. synthesized a hierarchically structured P2-type layered K<sub>0.6</sub>CoO<sub>2</sub> cathode which not only delivered a high specific capacity, but was also capable of cycling K<sup>+</sup> ions at reasonably high rates (13). On the anode side, a variety of materials such as graphite (14), hard carbons (15), soft carbons (16) as well as phosphorous-based alloys (17) have been explored in secondary K batteries. In contrast to this, the direct use of K metal as the anode would allow for superior specific capacity than carbonaceous, alloying, or intercalation compounds as the packing density of K atoms is the highest in its metallic form. However, similar to Li, the K-metal anode is observed to develop dendritic projections during the electrochemical plating-stripping processes, which occur when the battery is being charged and discharged. The growth of dendrites is associated with irreversible capacity loss, a reduced Coulombic efficiency, as well as drying and degradation of the electrolyte (18). Most importantly, these dendritic projections can pierce through the separating membrane and electrically short the battery, leading to a severe thermal runaway, which could result in a catastrophic fire hazard.

Kinetically, the nucleation and growth of metal dendrites is highly favorable during electrochemical plating and stripping processes. It is generally accepted that a higher current density (i.e., faster charge/discharge) would promote dendritic growth, since the diffusion-limited aggregation of dendrites should be favored under such conditions. In previous work (19, 20) on Limetal systems, we demonstrated that this is not always the case. In particular, we demonstrated a distinct regime in which the

### Significance

Historically, battery self-heating has been viewed negatively as an undesirable attribute. However, we report that battery selfheat, if properly controlled, can smoothen dendritic features in potassium metal batteries. This could open the door to high gravimetric and volumetric energy density potassium-ion batteries that could offer a sustainable and low-cost alternative to the incumbent lithium-ion technology.

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<sup>&</sup>lt;sup>1</sup>To whom correspondence may be addressed. Email: koratn@rpi.edu.

opposite was true, where at very high current densities ( $\sim 15 \text{ mA cm}^{-2}$ ), the internal self-heating of the battery triggers extensive surface diffusion of Li, which smoothens (heals) the dendrites. In this study, we investigate how K dendrites in K-metal batteries respond to selfheat. We discover that the process of self-heat-driven healing (smoothening) of dendrites is strikingly more effective in K as compared to Li metal. The parameter used to control the battery self- (Joule) heating is the operating current density (or chargedischarge rate) of the cell. Because K dendrites are far easier to heal when compared to their Li counterparts, the current density required to trigger the healing was an order-of-magnitude lower for K  $(\sim 1.5 \text{ mA cm}^{-2})$  as compared to that of Li metal ( $\sim 15 \text{ mA cm}^{-2}$ ). This markedly lower current density suggests that a smaller rise in temperature while cycling is required for self-diffusion assisted healing of K dendrites, which would make electrolyte degradation or damage to the separator less likely. Therefore, the thermally activated healing of K dendrites is not only more efficient, but also much safer, when compared to that of Li.

To uncover the mechanism as to why K dendrites heal much easier than Li, we used first-principles density-functional theory (DFT) calculations to estimate the extent of surface diffusion of K metal atoms by calculating activation energy barriers for surface diffusion via hopping and exchange diffusion mechanisms (20). Similar calculations were also performed for self-diffusion of Li. Further, we look at an Arrhenius picture to investigate K surface diffusion as a temperature-activated process and compare the results to that of Li (20). Our theoretical study reveals that the activation barrier for surface diffusion in K (~0.1 eV) is significantly lower than that in Li (~0.15 eV). Consequently, even at a moderately high temperature of ~50 °C, the rate constant of surface diffusion of K is about fivefold higher than that of Li at the same temperature. The drastically higher selfdiffusion for K as compared to Li metal explains why K dendrites are much easier to heal when compared to Li. We also show that K dendrites can be healed in a full-cell device that consists of a  $K_{0.6}CoO_2$  cathode and a K-metal anode.

Battery self-heating typically has a negative connotation; however, our results indicate that battery self-heat, if properly controlled, can smoothen dendritic features in K-metal batteries. This could lead to high-performance K-ion batteries that could offer a sustainable and low-cost alternative to Li-ion technology.

### Results

To study the morphology of the K-metal electrode after cycling, we tested K-K symmetric cells over a wide range of operating current densities (Fig. 1 A and B), ranging from low ( $\sim 0.01$ mA cm<sup>-2</sup>) to moderately high values ( $\sim 2$  mA cm<sup>-2</sup>). We imaged the surfaces of the K-metal foils used in the experiments by ex situ scanning electron microscopy (SEM). Shown in Fig. 1 C-J are the SEM images of the K-metal electrode surface after 50 cycles of charge and discharge at current densities of  $\sim 0.01$ ,  $\sim 0.1$ , ~0.5, ~0.75, ~1.5, and ~2 mA cm<sup>-2</sup>. As expected, large isolated hemispherical deposits (Fig. 1C) were observed after operation at a low current density (~0.01 mA cm<sup>-2</sup>). At such low current densities, the deposition of K is considered to be charge-transfer controlled (21). As the operation current density increases (Fig. 1 D-F), nuclei grow in a dendritic form and the deposition is diffusion controlled (21). The dendrites formed are more densely packed and their diameter decreases with increasing current density. However, with further increase in the current density  $(\sim 2 \text{ mA cm}^{-2})$ , the morphology of the K-metal surface appears to be smooth and nondendritic in nature (Fig. 1*H*). At a current density of  $1.5 \text{ mA cm}^{-2}$ , partial healing can be observed (Fig. 1*G*), where the individual dendritic structures seem to have fused (or merged) together. Cross-sectional images of the electrode cycled at ~0.01 and ~2 mA cm<sup>-2</sup> are shown in Fig. 1*I* and *J*, respectively. Due to their porous nature, deposition of platinum and ion milling of the dendrites leads to their structural collapse (Fig. 11).

However, the cross-sectional image clearly reveals a high degree of porosity, which is to be expected for the dendritic layer. By contrast, the cross-section of the K-metal electrode cycled at  $\sim 2 \text{ mA cm}^{-2}$  exhibited a compacted (or healed) sublayer in which the individual K dendrites have merged and fused together (Fig. 1*J*), which confirms the effectiveness of the healing phenomenon. These results are also consistent with the voltage profiles in Fig. 1*B*. The voltage profile of the cell cycled at  $\sim 0.5 \text{ mA cm}^{-2}$  is indicative of extensive dendritic growth and increasing cell impedance. By contrast, the cell cycled at  $\sim 2 \text{ mA cm}^{-2}$  exhibits high impedance initially, but the voltage profile stabilizes, which indicates that the dendrites formed in the initial cycles get healed over time.

We used first-principles DFT calculations to study the surfacediffusion characteristics of Li and K metal. To study surface diffusion, we consider both hopping and exchange mechanisms. In the hopping mechanism, we consider that the adatom moves from one equilibrium adsorption position to another (Fig. 2 *A* and *B*). The rate of diffusion is estimated by the calculated energy barrier along the path. The diffusion path is determined by comparing the adsorption energy of the adatoms on the highsymmetry sites of their, respective, most stable surface terminations. The adatom is allowed to relax in the direction perpendicular to the (001) surface. The adsorption energy (E<sub>ads</sub>) is calculated by subtracting the energy of the clean metal electrode without the adatom (E<sub>slab</sub>) and the energy of the single adatom (E<sub>atom</sub>) from the energy of the system with the relaxed adsorbate adatom (E<sub>sys</sub>), i.e., E<sub>ads</sub> = E<sub>sys</sub> - E<sub>slab</sub> - E<sub>atom</sub> (20).

The exchange, or the concerted displacement mechanism of diffusion involves the cooperative motion of several surface atoms. To determine the activation barrier in this mechanism, an exchange diffusion pathway (20) (i.e., the preferred adsorption site to the nearest surface neighbor, then to the next preferred adsorption site) is considered as follows. Adatom A sits originally in the fourfold hollow site, while surface atom B is one of its nearest neighbors on the (001) surface. Both atoms move cooperatively such that adatom A replaces surface atom B, while surface atom B becomes an adatom in the next fourfold hollow site. This is illustrated in Fig. 2*C* and has been adopted from the approach used in ref. 22. The nudged elastic band (NEB) method (23) was utilized to find the minimum energy path (MEP) and activation barrier in the exchange mechanism (Fig. 2*D*).

The minimum energy path for self-diffusion of both Li on Li (001), and K on K (001) in the exchange mechanism is hindered by an activation energy barrier ( $\sim 0.15$  eV for Li and  $\sim 0.1$  eV for K). This energy barrier for exchange is much lower than the corresponding barrier for the hopping mechanism. For example, in the case of K, the barrier for the exchange mechanism ( $\sim 0.1$ eV) is less than half the barrier for the hopping mechanism ( $\sim 0.23$  eV), and therefore we conclude that the exchange mechanism is the predominant mechanism for self-diffusion in K. This barrier of diffusion in K is also significantly lower than the barrier for both types of diffusion (i.e., exchange as well as hopping) in Li. Consequently, K exhibits a much higher rate of self-diffusion [calculated using the Arrhenius equation (24), Fig. 2E] when compared to that of Li. For example, at a temperature of ~50 °C, the rate constant of surface diffusion for K is about fivefold higher (Fig. 2E) than that of Li at the same temperature. While modeling effects of the solid electrolyte interface (SEI) and solvent (electrolyte) is challenging using DFT due to the system size and complexity, such work should be pursued as part of future studies.

## Discussion

The magnitude of the metal self-diffusion energy barrier has been proposed as a descriptor for occurrence of dendrite growth (25), and growth phenomena at interfaces are closely related to the diffusion coefficient (26, 27). Considering the link between



**Fig. 1.** Dendrite morphology in K-K symmetrical cells. (A) Schematic of a symmetric K-K cell. (B) Potential-time profiles for K-K symmetric cells operated at low and high current densities. SEM images depicting the surface morphology of the K-metal electrode in K-K symmetric cells cycled at different current densities: (C) ~0.01 mA cm<sup>-2</sup>, (D) ~0.1 mA cm<sup>-2</sup>, (E) ~0.5 mA cm<sup>-2</sup>, (F) ~0.75 mA cm<sup>-2</sup>, (G) ~1.5 mA cm<sup>-2</sup>, and (H) ~2 mA cm<sup>-2</sup>. Cross-sectional images of the K-metal electrode operated at (I) ~0.01 mA cm<sup>-2</sup> and (J) ~2 mA cm<sup>-2</sup> produced by FIB milling.

lower self-diffusion barrier and growth of smooth surface structures, we infer that K metal can present a relatively smooth surface with suppression of dendrite growth. This inference is consistent with our experimental findings as suppression of Kdendrite growth is clearly observed at current densities that provide sufficient thermal energy for self-diffusion. The predicted

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**Fig. 2.** First-principles DFT calculations of surface diffusion. Adsorption energy landscape for (A) Li adatom on Li (001) and (B) K adatom on K (001). (C) Snapshots of the atomic configuration along the MEP for self-diffusion with the adatom in a fourfold hollow in the exchange mechanism. (D) Activation energy barrier calculated by NEB method for the diffusion by exchange mechanism for Li and K. (E) In an Arrhenius picture, the diffusion rate constant ( $k^{STST}$ ) at a temperature T is computed using a simple approximate form (24) of STST, in which  $k^{STST} = n_p v_0 \exp[-(E_{saddle} - E_{min})/k_BT]$  (*Materials and Methods*). The variation of the diffusion rate constant with temperature for both Li and K is plotted.

temperature rise in the dendrites as a function of current density is provided in *SI Appendix*, Fig. S3 along with details of the thermal modeling approach (*SI Appendix*, Fig. S1). With electrical resistance of the electrolyte and SEI far exceeding that of the metal dendrite, it is assumed that Joule heating is predominantly in the electrolyte and SEI and that heat is transferred to the K-metal dendrite at the dendrite/SEI/electrolyte interface (*SI Appendix*, Fig. S2). The computational thermal modeling results indicate that temperatures on the order of 30–40 °C (in the K dendrites, *SI Appendix*, Fig. S3A) and 40–50 °C (in the electrolyte/SEI, *SI Appendix*, Fig. S3B) are possible at current densities of ~2.0 mA cm<sup>-2</sup>. Note that these temperatures are well below the melting temperature of K (~63.5 °C) or the onset temperature at which degradation of the electrolyte/separator (about 80–90 °C) would be initiated.

A thermal annealing control experiment was also carried out to confirm the thermally assisted surface diffusion mechanism for healing of the K dendrites. For this, cells were cycled at a current density of ~0.5 mA cm<sup>-2</sup> for about 200 h (50 chargedischarge cycles) to generate dense regions of closely spaced dendrites (SI Appendix, Fig. S4A). The cells were then thermally annealed at ~40 °C on a hot plate for up to 72 h. The annealing was carried out without opening the cells, to ensure that the annealing took place in the presence of the battery electrolyte. Inspection of these electrodes after thermal annealing by SEM (SI Appendix, Fig. S4 B and C) indicates diffused or merged surfaces and a smooth morphology that is similar to the electrodes cycled at high current density ( $\sim 2 \text{ mA cm}^{-2}$ , see Fig. 1*H*). Such healing of the dendrites in a high current density regime substantially reduces the risk of dendrite penetration through the separator, improving the safety of secondary batteries using K metal as the anode.

To analyze the structure/chemistry of the SEI of the K-metal anode run at low (~0.01 mA cm<sup>-2</sup>) and high (~2 mA cm<sup>-2</sup>) current densities, we carried out depth profiling (*SI Appendix*, Fig. S5) via X-ray photoelectron spectroscopy (XPS). O1s scans reveal the presence of C–O bond at about 530 eV, C = O bond at 531.8 eV, and CO<sub>3</sub><sup>2-</sup> at 533.5 eV. K2p scans indicate doublets corresponding to K-F (293.5, 295.8 eV) and K–O bonds (292, 295 eV). Additionally, a peak corresponding to K<sub>4</sub>X/K<sub>3</sub>X (290.8 eV), where X is a counterion, was also detected. In general, we found that much sharper peaks (*SI Appendix*, Fig. S5 *C* and *D*) were observed for the sample cycled at 2 mA cm<sup>-2</sup>, which suggests less diversity in the SEI composition. By contrast, the sample cycled at 0.01 mA cm<sup>-2</sup> exhibited more diffused and broader peaks (SI Appendix, Fig. S5 A and B), which is indicative of a more diverse SEI with significant contribution from multiple compounds. For example, the  $K_4X/K_3X$  (where X is a counterion) contribution is prominent at a current density of 0.01 mA cm<sup>-2</sup>, but is negligibly small at 2 mA cm<sup>-2</sup>. These observations can be explained based on reaction kinetics. At low current densities (e.g.,  $0.01 \text{ mA cm}^{-2}$ ), reactions with slow kinetics have sufficient time to complete as opposed to cycling at high current densities (such as  $2 \text{ mA cm}^{-2}$ ), where the plating and stripping of potassium dominates over reactions with slow kinetics. Thus, at high current densities, fewer compounds are present in larger amounts, resulting in sharp peaks in the XPS spectra. At low current densities, a more diverse set of compounds are present in relatively smaller amounts, which results in a broadening of the XPS response.

Another key observation was how the SEI composition changes with respect to its thickness. Sputter-down XPS of the potassiummetal anodes revealed a uniform distribution of compounds through the depth of the SEI for samples cycled at 2 mA cm<sup>-2</sup>. *SI Appendix*, Fig. S5 *C* and *D* indicates that there is virtually no change in the XPS K2p and O1s spectra with depth. The situation is different for samples cycled at 0.01 mA cm<sup>-2</sup>, with significant changes in the relative intensities of the XPS peaks with depth (*SI Appendix*, Fig. S5 *A* and *B*). The variation of the types and quantities of compounds through the thickness of the SEI on the potassium-metal anode cycled at 0.01 mA cm<sup>-2</sup> indicates increased nonuniformity in the SEI. On the other hand, at the healing current density of 2 mA cm<sup>-2</sup>, the SEI is far more uniform in the thickness direction when compared to the SEI that develops at low current densities.

To investigate the effect of current density on SEI thickness, we carried out electrochemical impedance spectroscopy on K-K symmetric cells cycled at low (0.01 mA cm<sup>-2</sup>) and high (2 mA cm<sup>-2</sup>) current densities (*SI Appendix*, Fig. S6). It is clear that the SEI resistance from intercepts of the high-frequency semicircles are lower for the cell cycled at 2 mA cm<sup>-2</sup> as compared to that cycled at 0.01 mA cm<sup>-2</sup>. Due to the much lesser resistance of the K-K cell cycled at 2 mA cm<sup>-2</sup>, the two semicircles representing charge transfer (CT) and SEI resistance tend to overlap

and cannot be distinguished. Therefore, for the 2-mA cm<sup>-2</sup> case, a single semicircle is used for fitting to obtain the total impedance (i.e., SEI + CT) of the cell. The SEI + CT resistance was calculated to be ~46.8  $\Omega$  (at 2 mA cm<sup>-2</sup>), which is considerably lesser than the SEI resistance of the anode cycled at 0.01 mA cm<sup>-2</sup> (~168.3  $\Omega$ ) with a dendritic morphology. This reduction in the resistance is indicative of a relatively thinner SEI for the K-metal foil that is cycled at the healing current density of 2 mA cm<sup>-2</sup> as compared to 0.01 mA cm<sup>-2</sup>.

Based on *SI Appendix*, Figs. S5 and S6 we conclude that the SEI that forms at the healing current density of 2 mA cm<sup>-2</sup> is far more uniform (i.e., less heterogeneous) and thinner than the SEI created at low current densities. It is well established that the nucleation of dendrites is exacerbated for a more heterogeneous and thicker SEI, due to nonuniform diffusion of K<sup>+</sup> through such layers. Consequently, in our system once the dendrites get healed (due to surface diffusion triggered by battery self-heat), they are less likely to renucleate due to the enhanced uniformity and

reduced thickness of the SEI layer that is formed at the healing current density.

To demonstrate the application of healing of K dendrites in a working secondary battery, we assembled a full cell (Fig. 3A) with K-metal foil as the anode and the P2-type layered  $K_{0.6}CoO_2$ (s-KCO) (13) as cathode. The s-KCO cathode possess micrometersized hierarchical structured spheres assembled from nano- or submicrometer primary particles. The nanosized primary particles assist with fast ion intercalation/deintercalation (SI Appendix, Table S1), while the microsized spheres minimize parasitic reactions and improve the volumetric energy density of the battery. These s-KCO cathodes not only maintained a high capacity with a low fade rate at a current density of  $\sim 500 \text{ mA g}^{-1}$ (13), but were also capable of being operated at the current densities (Fig. 3B) required to heal the dendrites. The full cells were cycled at low current density of ~0.5 mA cm<sup>-2</sup> (Fig. 3C) and in another experiment were cycled at low current density of ~0.5 mA cm<sup>-2</sup> with bursts of higher current density (~2 mA cm<sup>-2</sup>)



**Fig. 3.** Dendrite healing in a full cell with K metal as anode and s-KCO as cathode. (*A*) Schematic of the full-cell device. (*B*) Voltage profiles of the s-KCO|K cell operated at low and high current densities. Cycle stability of the full cells indicating specific charge capacity (red) and Coulombic efficiency of KCO (blue) when cycled at (*C*) low current density ( $\sim$ 0.5 mA cm<sup>-2</sup>) and (*E*) low current density ( $\sim$ 0.5 mA cm<sup>-2</sup>) with bursts of high current density ( $\sim$ 2-mA cm<sup>-2</sup>) cycles. SEM images of the K-metal electrode after cycling at (*D*) low current densities ( $\sim$ 0.5 mA cm<sup>-2</sup>) exhibit a dendritic surface morphology, while the surface of the K metal after cycling at (*F*) low current density ( $\sim$ 0.5 mA cm<sup>-2</sup>) with bursts of high current density ( $\sim$ 2 mA cm<sup>-2</sup>) cycles is devoid of any distinct dendritic projections.

cycles (Fig. 3*E*) to study the dendritic morphology on the cycled metal anode. Ex situ SEM images of the K-metal anode after cycling reveal a rough, dendritic surface at low current densities (~0.5 mA cm<sup>-2</sup>) (Fig. 3*D*). However, the surface of the K-metal anode cycled with bursts of higher current densities (~2 mA cm<sup>-2</sup>) was observed to have a smooth surface (Fig. 3*F*), due to healing of the K dendrites by Joule-heating-assisted surface diffusion, consistent with the observations made in a symmetric cell system. As expected, the cell cycled at low current density (Fig. 3*C*) has a lower average Coulombic efficiency (~96.43%) than the cell cycled at low current density (Fig. 3*E*) healing cycles (~98.92%).

It should be noted that the melting of potassium takes place at a much lower temperature (63.5 °C) as compared to lithium (180.5 °C). However, at a current density of  $\sim 2$  mA cm<sup>-2</sup>, melting does not take place in our potassium battery. The typical voltage profile at this current density is shown in Fig. 1B. During the dendrite growth as well as healing process, the voltage profile shows large fluctuations (or spikes) that are associated with the changing morphology of the dendritic surface and the SEI layer. After the healing is completed, a stable voltage profile is observed. As is evident from Fig. 1B, it takes about 30 h for the potassium surface and SEI to stabilize and heal. Such timescales are not consistent with a melting process, which would proceed much more rapidly, if the dendrite temperature were to exceed the melting point of potassium. On the other hand, surfacediffusion-induced healing is consistent with the timescales observed in our experiments. Further, our thermal modeling (SI Appendix, Fig. S3) predicts maximum dendrite temperatures of ~40 °C at an operating current density of ~2 mA cm<sup>-2</sup>. This is well below the melting temperature of potassium metal. The heating (annealing) of the coin cell on a hot plate at ~40 °C also supports the surface-diffusion hypothesis, since it takes over 36 h for the healing to be completed (SI Appendix, Fig. S4), which is comparable to the timescales in the electrochemical test (Fig. 1B). These results indicate that dendrite healing is a surface diffusion rather than a melting process.

It is possible that while healing the dendrites, the battery management system (BMS) could accidently malfunction and apply current densities that are much larger than  $2 \text{ mA cm}^{-2}$ . In such a scenario, could melting of the potassium-metal anode be a possibility? Certainly, this could take place in a K-K symmetrical cell, since in such a cell the current density can be raised to an arbitrarily large value, at which point the temperature rise in the K-metal foil could exceed the melting temperature, resulting in catastrophic failure. However, this is not the case in a practical full-cell configuration. Among cathodes for nonaqueous KIBs, s-KCO offers among the best high-rate capabilities reported to date (13). However, even the s-KCO electrode (which is optimized for high-rate operation) is unable to operate effectively above 2 mA cm<sup>-2</sup> current density as shown in *SI Appendix*, Fig. S7. At a current density of 2 mA cm<sup>-2</sup>, we predict maximum dendrite temperatures of about 40 °C based on our thermal modeling (SI Appendix, Fig. S3), which is significantly below the melting point of potassium metal. Other high-performing cathodes (SI Appendix, Table S1) for potassium-ion batteries are also unable to operate at current densities above  $2 \text{ mA cm}^{-2}$ . Thus, in our practical full-cell device, we do not cycle and more importantly even in the event of a BMS failure/malfunction, we cannot cycle at rates that might lead to melting of potassium. Further, since the capacity of the s-KCO drops to almost zero at current densities such as 5 mA cm<sup>-2</sup>, increasing current densities beyond 2 mA cm<sup>-2</sup> for the s-KCO cathode would not aid in dendrite healing on the K-metal anode.

The full-cell tests in Fig. 3 were conducted with ~0.8 M KPF<sub>6</sub> in dimethyl ether (DME) as the electrolyte. We also assembled K-K symmetric cells in an electrolyte of ~0.8 M KPF<sub>6</sub> in DME to confirm that the healing mechanism still applies in the ether-

based electrolyte. SEM images of the cycled K-metal anodes at varying current densities is shown in *SI Appendix*, Fig. S8. The dendrite evolution with current density is very similar to the results shown in Fig. 1 for the carbonate-based electrolyte. At current densities of  $\sim 2 \text{ mA cm}^{-2}$ , a smooth surface indicative of dendritic healing was observed. From these results, we conclude that the K-dendrite healing phenomena applies to both carbonate as well as ether-based electrolytes.

To summarize, we have studied how K dendrites respond to self-heat and compared our results to that of Li. Testing of symmetric cells indicates that the self-heating–driven healing of dendrites is far more effective in K as compared to Li metal. This enables dendrite healing to take place at an order-of-magnitude lower current density for K relative to Li. Detailed DFT calculations were used to explain the underlying reason for this behavior. It was found that the energy barriers for self-surface diffusion in K are much lower than in Li metal, which explains why K dendrites are easier to heal when compared to their Li counterparts. Finally, we show that self-heating–induced healing of the K-metal anode can also be accomplished in a full-cell setting, which indicates that this healing concept has important practical implications.

### **Materials and Methods**

Electrode Preparation. All procedures were carried out in an Ar-filled glovebox (MBraun Labstar). For the synthesis of s-KCO, ~0.95 g of CoCl<sub>2</sub>·6H<sub>2</sub>O was added into a solution containing ~20 mL of  $H_2O$ , ~55 mL of glycerol, and ~2.5 g of urea at room temperature under stirring. After stirring for  $\sim$ 2 h and making sure all of the chemicals were dissolved, the mixture was transferred to an ~100-mL Teflon-lined stainless-steel autoclave and reacted in a laboratory oven at ~180 °C for ~12 h. The precursors (CoCO3) were collected by centrifugation and washed with water and ethanol several times and dried at  $\sim 80$  °C overnight. The as-obtained CoCO<sub>3</sub> microspheres were calcined at ~500 °C for ~4 h in air to obtain the  $Co_3O_4$  microspheres. Then ~3 mM of Co $_3O_4$ , together with ~6 mM of KOH pellets, were dispersed in  ${\sim}1$  mL of  $H_2O.$  After being homogeneously mixed, the suspension was dried at  $\sim 80$  °C overnight. Finally, the solid mixture was preheated at ~350 °C for ~2 h and ~700 °C for ~10 h in an  $O_2$  environment to obtain the P2-type  $K_{0.6}CoO_2$  microspheres. After natural cooling, the temperature was held at  $\sim$ 200 °C before the samples were collected in an argon-filled glovebox to prevent contamination from moisture in the air. To prepare the working electrode, the as-synthesized P2-type  $K_{0.6}CoO_2$  (s-KCO), super-P carbon black, and polyvinylidene fluoride binder with a mass ratio of ~5:1:1 were hand milled with an adequate amount of N-methyl 2-pyrrolidone into a homogeneous slurry using a pestle and mortar under an argon atmosphere. The slurry mixture was coated onto an Al-foil current collector and then dried at ~100 °C for ~12 h under vacuum. The mass loading of the active materials for the electrode was  ${\sim}1.0~\text{mg}~\text{cm}^{-2}.$ 

Electrochemical Measurements. Arbin BT2000 was used to run all galvanostatic charge/discharge and plating/stripping tests. To assemble K/K symmetric cells and s-KCO/K full cells, 2032-type coin cells were used. For the K/K symmetric cells, potassium metal (99.5% trace-metal basis, Sigma-Aldrich) was used both as anode and cathode and  $\sim$ 0.8 M KPF<sub>6</sub> in EC:DEC (1:1 vol%) was used as the electrolyte. For the s-KCO/K full cell, potassium metal was used as the anode, while s-KCO (13) was used as the cathode with  $\sim 0.8$  M KPF<sub>6</sub> in DME as the electrolyte. K/K-symmetric cells with ~0.8 M KPF<sub>6</sub> in DME were also assembled. The salt (KPF<sub>6</sub>) and solvents (EC, DEC, and DME) were purchased from Sigma-Aldrich. The symmetric cells were cycled at various current densities with same cycle times (2-h charge, 10-min rest, 2-h discharge, 10-min rest). For the s-KCO/K cell, galvanostatic charge/discharge cycles were performed over the voltage range from 1.7 to 3.75 V (vs. K/K<sup>+</sup>). The capacity was normalized to the active mass loading of s-KCO. The current densities mentioned are with respect to the K-metal anode. Celgard 2340 were used as the membrane separator in all of our testing.

**Electrode Characterization.** The cells were opened in the Ar-filled glovebox to procure the cycled K-metal electrode. The electrode was washed with DEC solvent to remove any salt precipitates and dried. The K electrode was then sealed in an Ar-filled container and transferred for further characterization. K dendrites were imaged using the Carl Zeiss Supra 55 field-emission scanning electron microscope. An aperture of ~30  $\mu$ m and beam energy of ~5 kV was

used. The cross-section of the sample was obtained by gallium focused ionbeam (FIB) sputtering at ~30 keV using FEI VERSA three-dimensional dualbeam system. Coarse sputtering was carried out at ~15 nA and final cleaning of the cross-section surface was carried out at ~1-nA beam current. Ionbeam-deposited platinum at the top surface protects the sample surface from damage due to sputtering at higher ion-beam currents. Secondary electron images of the cross-section were obtained by incident electron beam at ~10 keV and the sample at a ~52° tilt. SEI characterization was carried out by using XPS AI K $\alpha$  radiation (~1486 eV) in a PHI 5000 Versaprobe system (20).

**First-Principles Calculations.** The Vienna ab initio simulation package program was used for the first-principle DFT (28) calculations. Core electrons were described by the projector augmented-wave pseudopotentials (29), and exchange-correlation energies of electrons used the Perdew, Burke, and Ernzerhof functional (30) for generalized gradient approximation. The plane-wave energy cutoff for different interfaces (for all of the calculations) was taken as 550 eV. All ions were fully relaxed during the structural optimization until the total energy was converged within  $10^{-5}$  eV per cell, and the total energy was calculated with the linear tetrahedron method with Blochl corrections. The electrode surfaces are modeled by five-layer slabs.

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The vacuum layer for the slab models is around 11.5 Å. Adsorption energies and diffusion paths have been determined within a  $4 \times 4$  geometry using a  $5 \times 5 \times 1$  k-point grid. For all adsorption calculations, the atoms of the two uppermost surface layers have been allowed to relax in all directions (20).

We calculated the rate constants using a simple approximate form (24) of transition-state theory (STST), in which  $k^{\text{STST}} = n_p v_0 \exp\left(-\frac{E_{diff}}{k_BT}\right)$  where  $n_p$  is the number of possible exit directions,  $v_0$  is the harmonic frequency,  $E_{diff}$  is the activation energy barrier for the diffusion process,  $k_B$  is the Boltzmann constant, and T is the temperature.  $n_p = 4$  due to the fourfold symmetry of the diffusion mechanism. Here the rate constant has been calculated for the exchange mechanism, and the harmonic frequency has been approximated from a harmonic fit to the potential energy curve for the exchange mechanism (20).

Data Availability. All relevant data are provided as Datasets S1–S16.

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