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Rapid reversible electromigration of intercalated K ions within individual MoO₃ nanobundle

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Rapid and reversible electromigration of intercalated K ions within an individual layered single crystalline K_xMoO₃ nanobundle is observed. When an electric current was applied to a K_xMoO₃ nanobundle, the K ions migrated readily and rapidly in the flowing direction of electrons within the nanobundle and accumulated near an electrode. Upon reversal of the applied current, the accumulated K ions near one electrode were driven back and gathered near the opposite electrode. This observation is attributed to the unique structure of K_xMoO₃ where K ions occupy O vacancies in the nanobundle and the location of K ions is exactly the channel of high current density within the nanobundle. The duration required to induce significant accumulation of K ions and relaxation time of accumulated ions were significantly shorter than the value reported in other interstitial systems. The reversible ion movement was repeated for hundred times and remarkably there were no obvious sign of structural damage in the nanobundle. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4774244>]

I. INTRODUCTION

Electromigration describes the forced atomic or ionic motion driven by electric field and associated electric current.^{1–3} The net driving force causes the atoms/ions to move from its original position. In an interstitial system with applied driving force in the form of electron wind force, small interstitial ions can jump from one interstitial site to neighbouring ones while large atoms can move by position exchange with neighbouring vacancies.^{3–5} In the event of high current density, a great amount of electrons scattering with atoms/ions causes electromigration, thus, the phenomenon is mainly studied in metals or other materials with low resistivity.^{3,4,6–9}

With layered crystalline structure, MoO₃ presents a wide range of sites for ions intercalation. In particular, Li ions intercalation into MoO₃ was successfully demonstrated and the layered structure was found to be preserved during Li⁺ insertion/extraction process.^{10,11} When the current density within intercalated MoO₃ is high enough to provide significant electron wind force, intercalated ions could migrate along layers. Compared with the high current den-

sity in bulk metal where electromigration takes place (10^3 – 10^4 A cm^{−2}),^{1,3} the current density of lithiated MoO₃ bulk (Li_{0.25}MoO₃ 1 A cm^{−2})¹² and lithiated MoO₃ nanobelt (10^{-3} A cm^{−2})¹³ is too low to cause electromigration. Some molybdenum bronze possess high conductivity, but insertion of ions in the bronze gives rise to substantial structural distortion. Such as blue potassium bronze (K_{0.3}MoO₃), the compound becomes infinite sheets with the adjacent sheets held together by potassium ions.¹⁴ The K ions bound by seven or ten oxygen atoms to hold the adjacent sheet can hardly move around. Consequently, the electromigration phenomenon of intercalated ions in layered MoO₃ structure has not been observed before.

We have successfully synthesized K ions intercalated MoO₃ (K_xMoO₃) nanobundle with the integrity of the layered structure remaining intact. Details of the synthesis, characterization, and electrical properties of the nanobundle were reported previously.¹⁵ The material displayed semiconductor-like behavior with dramatic enhancement of the electric conductivity from 10^{-6} S m^{−1} of MoO₃ to 24 S m^{−1} upon potassium uptake. For samples (pure and K-intercalated MoO₃) with a length of 10 μm and biased at 5 V, the current densities were measured to be 5×10^{-5} A cm^{−2} and 10^3 A cm^{−2}, respectively. The high conductivity of the K-intercalated MoO₃ nanobundle excludes the

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possibility of ionic conductivity which is usually low at room temperature.^{16,17} Experimental measurement of $K_x\text{MoO}_3$ nanobundle reveals the significant amount of oxygen vacancies in the structure. Theoretical simulation shows that hopping barrier of intercalated K ions is 0.23 eV.¹⁵ The high current density, the preserved layered structure, the significant amount of oxygen vacancies for position exchange, and the low hopping barrier suggest the possibility that K ions can migrate along the layers readily when they are driven by electron wind force.

In this work, we demonstrate a surprising reversible electromigration of the intercalated K ions in $K_x\text{MoO}_3$ nanobundle driven by electron wind force. We studied the effect of application of an electric current on the nanobundle. We found that there was a significant variation in the distribution of K ions in $K_x\text{MoO}_3$ nanobundle before and after the application of current. This implied the electromigration of K ions within the nanobundle and the direction of the migration corresponded exactly to the flowing direction of electrons. Upon the reversal of current, the accumulated K ions near one electrode could be driven back and gathered near the opposite electrode. By controlling the direction of the electric current, the movement of K ions along layers was shown to be reversible. Most notably, the electromigration only took a matter of seconds. Compared with the reported long duration to induce significant variation of ion distribution,^{18,19} the K ions in $K_x\text{MoO}_3$ nanobundle migrated in a much shorter time. Moreover, repeated reversible electromigration of the K ions did not result in any changes in morphology of nanobundles.

II. RESULTS AND DISCUSSION

After the growth of $K_x\text{MoO}_3$ nanobundles,¹⁵ individual $K_x\text{MoO}_3$ nanobundle was transferred to a Si substrate with a

100 nm SiO_2 layer. Patterned electrodes of 10 nm Cr and 500 nm Au were fabricated via standard photo lithography and sputtering of metals. Figure 1(a) shows a scanning electron microscope (SEM) image of a typical segment of nanobundle between two electrodes. The length of the segment of nanobundle is around $10\ \mu\text{m}$ and the growing direction of nanobundle is [001]. The energy disperse X-ray spectroscopy (EDX) (EDX in FESEM, JEOL JSM-7600 F) of selected spots on nanobundle was measured to explore the distribution of K ions in $K_x\text{MoO}_3$ nanobundle before and after the application of electric current. In these experiments, the electrical measurements were carried out using Keithley 6430 Sub-fA Remote SourceMeter. Figure 1(b) shows a typical EDX spectrum of nanobundle, the Au peak comes from gold electrode, the Si peak is from Si/ SiO_2 substrate, the Mo and K peaks come from nanobundle. From the area of the peaks, the value and error of atomic percentage ratio of K over Mo were calculated. In MoO_3 structure, each of the lattice Mo atoms is tightly bonded to the surrounding six O atoms and thus can hardly move, while the fully ionized intercalated K atoms are not completely trapped. Electromigration occurs primary through the untrapped interstitial atoms.^{3,20} Consequently, it is reasonable that Mo atoms remain stable and uniformly distributed in the MoO_3 lattice during electromigration process. Hence the atomic percentage ratio of K over Mo was used to study the distribution of K atoms in the following experiment.

Before the application of current, the EDX spectra of selected positions along nanobundle in SEM were measured. The black curve in Figure 1(c) shows the log scale of EDX intensity measurement in the square box highlighted in Figure 1(a) and the atomic percentage ratio of K over Mo versus distance away from electrode 1 is shown in black squares in Figure 1(d). The black line drawn to the data was meant to guide the eyes. The similarity in the magnitude of atomic

FIG. 1. (a) SEM image of a typical segment of nanobundle between two gold electrodes. (b) Typical EDX spectrum of $K_x\text{MoO}_3$ nanobundle between electrodes. (c) Log scale of EDX intensity measurement from the area highlighted by black square in (a) before (black curve) and after (red curve) application of electric current. (d) Measured atomic percentage ratio of K over Mo versus distance away from electrode 1 in the sample before applied bias voltage (black square), after applied positive bias voltage (red square), and after applied negative bias voltage (blue square).

ratio along the nanobundle reveals the uniformly distributed K ions in nanobundle before applying the current. Upon the application of a positive bias voltage (+5 V) for 30 min, the current flow from electrode 1 to electrode 2 as shown (black arrow) in Figure 1(a). The red curve in Figure 1(c) shows the logarithmic scale of the EDX intensity measurement in the same square box. The area of Mo peak in two curves is almost the same but the area of K peak increases after the application of the electric current. It denotes the increased amount of K atoms in the square box. The red squares in Figure 1(d) show the measured atomic percentage ratio of K over Mo at different distances away from electrode 1 after applied current. Near electrode 1, the atomic ratio is around 20.5%, while the value decreases to 16.5% for regions close to electrode 2. The accumulated K ions near electrode 1 and the depletion near electrode 2 show that K ions from negative electrode migrate towards positive electrode along the direction of electron flow (i.e., opposite to the electric current). The sample was subsequently subjected to a reverse applied bias voltage (−5 V) for 30 min, current flow from electrode 2 to electrode 1. The blue squares in Figure 1(d) describe the resultant distribution of atomic percentage ratio of the sample. The high ratio near electrode 1 in red squares decreases to 16% in blue squares, and the ratio near electrode 2 increases to 20%. It reveals that the accumulated K ions near electrode 1 are flushed back by electron wind force in opposite direction and accumulated near electrode 2 instead.

During the EDX measurement, although the majority of detected X-ray comes from the small area centered at selected spot, the extended beam profile of the e-beam results in some EDX contribution of surrounding region. As shown in the EDX curve (Figure 1(b)), due to the large area of surrounding Au electrodes, although the electron beam was aimed at the middle of nanobundle, a small peak of Au was detected. Consequently, the measured atomic percentage was the weighted average value of the area centered at selected spot instead of the precise value at the spot. Taking into account the spreading of electron beam, the value we obtained is thus an underestimation. Meanwhile, we could not carry out EDX analysis and apply the current simultaneously. The EDX measurement was carried out around 30 min after the application of the electric current. We observed that the accumulated K ions gradually dispersed overtime and this is driven by concentration gradient force. Thus, the measured concentration of K ions is lower than the value

obtained immediately after the application of current. Although the accumulation effect is underestimated considering these two factors, the EDX analysis does clearly show the trend of reversible electromigration of K ions driven by electron wind force.

Beside the high current density that guarantees the electromigration of K ions along layers, some unique structural properties of $K_x\text{MoO}_3$ nanobundle favor the electromigration process. According to experimental measurement and theoretical modeling, K atoms likely occupy the oxygen vacancy sites in the lattice.¹⁵ The schematic atomic structure is shown in Figure 2(a). Between the MoO_3 layers, the dangling O atoms are removed as O vacancies in the lattice and K atoms occupy these vacancy sites. These K atoms are aligned in the channel formed by O vacancies along [001] direction. The experimental result shows that the amount of O vacancies is larger than that of K atoms, suggesting that not all vacancy sites are occupied. Figure 2(b) is the zoom-in image of the area highlighted by black square in Figure 2(a). Two kinds of Mo atoms are notable, one with O vacancy (reduced Mo atoms, green ball) and the other without (unreduced Mo atoms, blue ball). The ionization of the K atoms at vacancy site gives rise to the reduction of the adjacent Mo atoms, leading to electron population in the conduction band. Therefore, the high current density arises solely from the reduced Mo atoms, which are aligned in the [001] direction as shown in Figure 2(b). While the rows in which the Mo atoms remain in the high oxidation states are still semi-conductive due to lack of electron occupation in the conduction band. Consequently, when the current is applied in [001] direction, electrons mainly flow along these rows with the reduced Mo atoms. This is exactly the position where K atoms reside. Thus, K atoms can be mobilized by a great amount of flowing electrons along the channel formed by the layered structure. Meanwhile, these fully ionized K ions are weakly bound to the surrounding O atoms in the lattice. Theoretical simulation reveals that the hopping barrier of intercalated K ions is 0.23 eV, which is comparable with electromigration activation energy in conventional electromigration.^{21–23} Moreover, a significant amount of oxygen vacancies available in the structure for position exchange ensures facile diffusion of K ions.^{3,5} All these factors contribute to the ease of electromigration of K ions in $K_x\text{MoO}_3$ nanobundles.

Under the influence of electron wind force, K ions are accumulated near the electrode and such accumulation

FIG. 2. (a) Structure of K enriched MoO_3 nanostructure. (b) Zoom-in image of area highlighted by black square in (a).

introduces additional electric potential to the nearby electrode. After the applied current was removed, the electric potential between two electrodes induced by the accumulated K ions was measured and denoted as remnant voltage. To probe the properties of the remnant voltage, the sample was applied at different bias voltage for 20 s and the remnant voltage was measured immediately the moment applied bias was removed. The black, red, and blue curves in Figure 3(a) show the measured remnant voltage after bias voltage of +7 V, +5 V, and +2 V was applied, respectively. The measured positive remnant voltage is consistent with the observation that K ions migrate towards positive electrode when positive bias voltage is applied. The significant starting remnant voltage (56 mV after applying 7 V bias for 20 s) indicates that great amounts of K ions are indeed accumulated upon the application of electric current. The schematic figures in Figure 3(b) display the measurement process. Upon the application of the positive bias voltage, electrons flow from negative end to positive end and drove K ions to positive electrode. Immediately after the removal of the bias, the voltage between two electrodes was measured. Since accumulated K ions were near positive electrode, the recorded remnant voltage was positive. Comparison among these three curves reveals that a higher starting remnant voltage was measured when a larger bias voltage was applied. Figure 3(c) shows the measured starting remnant voltage after different bias voltage was applied. The experiment data were well fitted by exponential curve. A higher bias voltage induces a larger current density and higher electron energy and, consequently, enhances the electron wind force. With larger driving force, more K ions are accumulated, which provides higher remnant voltage. To further identify the effect of key parameter—current density, the measured starting remnant voltage versus applied bias current was plotted in Figure

3(d). Clearly, the starting remnant voltage increases linearly with bias current denoted by red fitting line. It suggests that the amount of accumulated K ions linearly depends on current density. A kink at $3 \mu\text{A}$ is observed. The measured starting remnant voltage was quite low and only increased a bit when bias current was lower than $3 \mu\text{A}$. It is attributed to the fact that certain energy is required to dislodge K ions and the significant remnant voltage could be observed only when large amount of ions are driven. When low current density ($<3 \mu\text{A}$) is applied, the energy provided by electron momentum transfer is not strong enough to drive K ions to the electrode. The threshold bias current denotes the hopping barrier of K atoms in the structure, and the low threshold bias current is indicative of the small activation energy of K atoms in the structure, which is consistent with the theoretical calculation of hopping barrier of K atoms (0.23 eV). The green curve in Figure 3(a) shows the measured remnant voltage after negative voltage of -2 V was applied. The negative remnant voltage suggests that K ions migrate towards negative electrode and are accumulated over there. The measured remnant voltage after applying positive and negative bias voltages proves that K ions migrate in the direction of electron flow driven by electron wind force.

Driven by concentration gradient force, the accumulated K ions diffuse back toward the nanobundle. As the concentration of accumulated K ions decreases with time, the remnant voltage decreases as well. The exponential fitting of black, red, and blue curves in Figure 3(a) shows that the decay time of remnant voltage is around 20 s. The results indicate a very short relaxation time for accumulation of K ions, in contrast to the previously reported system where the relaxation of accumulated ions upon removal of the bias takes a few hours.^{8,19} The short decay time reveals the facile diffusion of K ions along the channel formed by the layered

FIG. 3. (a) After bias voltage (7 V, 5 V, 2 V, and -2 V) was applied for 20 s, remnant voltage between two electrodes was measured with time. (b) Schematic figure shows remnant voltage measurement process. (c) Measured starting remnant voltage after different bias voltage was removed. (d) Measured starting remnant voltage after different bias current was removed.

structure. When accumulated K ions disperse in the same direction, the decay time and the pattern of curve are similar as shown in the black, red and blue curves in Figure 3(a). On the other hand, when accumulated K ions disperse in different directions, the decay time and the pattern of curve are different as shown in the black and green curves in Figure 3(a). This difference can be attributed to different history of the applied current in both directions and the random ion-vacancy position exchange. In addition, the channels, along which the K ions move, are not symmetrical in both ends. Hence even though the same current is applied for the same period in both directions, the distribution of accumulated K ions are different and the ways these accumulated ions disperse are also different. It leads to the varied amplitude of starting remnant voltage and the decay patterns of remnant voltage in opposite directions. For the same reasons, the decay time of each device is different from each other. But the values of decay time in all devices are smaller than 40 s, significantly lower than the reported relaxation time of accumulated ions.^{8,19}

As described in previous report,¹⁵ current density in the nanomaterial greatly increases with temperature (30 times with temperature increases from 25 °C to 200 °C), and the diffusion coefficient increases with temperature as well. Both factors greatly enhance the amount of K ions being driven. Due to the limitation that around 1.5 s is required to switch between different functions (as source and as voltmeter) in the equipment, and more K ions diffuse back during the interval as temperature increases, the starting remnant voltage versus temperature could not be systematically studied. However, the temperature dependence could be studied by focusing on two factors, current density and diffusion coefficient. The effect of current density was systematically studied as shown in Figure 3(d). The effect of diffusion coefficient under different temperatures could be studied by decay of remnant voltage.

The sample was mounted on heating stage and the remnant voltage measurement was repeated under different temperatures after bias voltage 2 V was applied for 20 s. To better characterize the diffusion coefficient under different temperatures, the maximum remnant voltage values were normalized. The three curves (blue, cyan, and green curves) displayed in Figure 4(a) correspond to normalized remnant voltage versus time under temperature of 25 °C, 37 °C, and 55 °C, respectively. Obviously, as temperature increases,

remnant voltage decays faster and faster. These three curves were exponentially fitted, and the decay time are 5.6 s, 2.1 s, and 0.5 s, respectively. The decreasing decay time suggests the increase of diffusion coefficient in the material as temperature increases. The decay time under different temperatures was recorded and plotted versus temperature in Figure 4(b). The data were well fitted by an exponential function and showed that the decay time of remnant voltage exponentially decreases as temperature increases with the equation $\tau = \tau_0 e^{-T/T_0}$, τ is the decay time, T is the absolute temperature, T_0 is the decay constant with the value around 12.7 K. Considering the fact that given a fixed length, the diffusion time is inverse proportional to diffusion coefficient, thus, the diffusion coefficient (D) of K ions in the structure increases exponentially with temperature in the measured temperature region, $D = D_0 e^{T/T_0}$ with constant T_0 around 12.7 K.

In interstitial system, long period (10^3 – 10^4 s) is required to observe significant concentration change of interstitial atoms upon electromigration.^{18,19} To study the time dependence of electromigration of intercalated K ions in MoO₃ nanostructure, same bias voltage (+3 V) was applied to the sample for different durations and the remnant voltage was measured immediately the moment bias voltage was removed. Due to the system limitation, the minimum period of the applied bias voltage was around 10 s. The red line in Figure 5(a) shows the measured remnant voltage versus time after bias voltage +3 V was applied for 10 s, and the starting remnant voltage is 18.7 mV. The black line in Figure 5(a) shows the remnant voltage versus time after bias voltage +3 V was applied for 100 s, and the starting remnant voltage is 23.5 mV. Applying similar bias voltage for a longer duration, e.g., 3000 s, the starting remnant voltage is around 24–25 mV. The small variation of starting remnant voltage implies that the accumulation of K ions becomes saturated with no additional K ions accumulated near the electrode. We assume that the initial electron wind force is much larger than the concentration gradient force and electrostatic force. This results in rapid accumulation and a significantly enhanced remnant voltage of 18.7 mV for the initial 10 s. With a longer period of current applied and more K ions accumulated, the net force on K ions gradually decreases and eventually diminishes without any net K ion accumulation. Thus, the starting remnant voltage only increases by 4.8 mV between 10 s and 100 s and is enhanced slightly (<1 mV) in the period from 100 s to 3000 s. The short duration (10 s)

FIG. 4. (a) After bias voltage 2 V was applied for 20 s, normalized remnant voltage between two electrodes was measured with time under different temperature, and (b) the exponential decay time of remnant voltage under different temperatures.

FIG. 5. (a) After bias voltage (+3 V) was applied for 10 s and 100 s, red and black curve show measured remnant voltage versus time, respectively. After bias voltage (-3 V) was applied for 100 s and then bias voltage (+3 V) was applied for 10 s, blue curve shows measured remnant voltage. (b) Schematic image describes the reversible electromigration process. (c) Current increased with time when bias voltage (+2 V) was applied in sample without bias voltage applied before (black line) and with bias voltage (-2 V) applied before (blue line).

required to achieve significant accumulation of K ions is consistent with the short relaxation time (30 s) of remnant voltage as shown in Figure 3(a), both values indicate the high diffusivity of K ions in the structure. The duration is much shorter than the time (10^3 – 10^4 s) required for the interstitial systems reported previously.^{18,19} It should be noted that in the previous reports, only small intercalated ions, such as Li^+ and H^+ , were studied, while in our system, the size of intercalated ion K^+ is significantly larger.

The time dependent electromigration relies on the history of applied current on nanostructure. We applied negative voltage -3 V for 100 s, upon the removal of the negative bias voltage, positive bias voltage +3 V was immediately applied for 10 s and the remnant voltage was measured as shown in blue curve in Figure 5(a). The starting remnant voltage was 1.2 mV, which is significantly lower than the starting remnant voltage (18.7 mV) when no bias voltage was applied before the application of positive voltage. The schematic figures in Figure 5(b) describe the process. Due to the long duration of negative bias voltage applied, great amounts of K ions are accumulated near negative electrode. When positive bias voltage was applied, for the same direction of electron wind force and concentration gradient force, accumulated K ions were quickly driven back and aggregated near positive electrode. As a result, the K concentration near positive electrode is higher than that near negative electrode and the measured remnant voltage is positive. However, it takes time to move K ions from negative side to positive side. Consequently, in the same duration (10 s), the measured starting remnant voltage (1.2 mV) is lower than the value (18.7 mV) when K ions were moved from uniform distribution to positive end. When longer duration (20 s) of positive voltage (+3 V) was applied, the measured remnant voltage versus time was the same as red curve in Figure 5(a) with starting voltage around 19 mV. The subsequent experiments indicate that when higher negative voltage (-5 V) was applied for 100 s, the applied positive voltage (+3 V) for 10 s was insufficient to change the sign of remnant voltage (the measured remnant voltage was still

negative). A longer duration or a larger positive bias voltage could drive more accumulated K ions back and make the remnant voltage positive. In general, the experiment shows that K ions are accumulated rapidly at the beginning when current is applied and accumulated ions could be driven back and gather in the other end when the current in opposite direction is applied. The distribution of accumulated ions depends on the duration and amplitude of the applied bias voltage and the history of applied bias voltage. After the reversible ion movement was repeated for hundred times, the reversible migration of K ions was still observed in remnant voltage measurement and, in particular, no expansion, void, and cracks in the nanobundle were observed. The unchanged morphology and the existence of reversible electromigration suggest that the MoO_3 layered structure is highly stable.

During the application of current, K ions are driven to one end. The accumulated K ions impose an additional voltage and thus influence the current. Positive bias voltage +2 V was applied to the sample and current was measured as shown in black curve in Figure 5(c). The current starts from 29.5 nA and increases sharply in the first few seconds. Then the slope gradually decreases, and finally the current reaches the equilibrium value of 37.5 nA. The increased current is due to the additional electric potential induced by accumulated K ions and the stable current suggests that the concentration distribution of K ions is equilibrated under electrostatic force, electron wind force, and concentration gradient force. The sharp increase of the current in the first few seconds reflects the fast increase of additional voltage which is induced by the rapid accumulation of K ions at the beginning as discussed above. Subsequently, negative bias voltage -2 V was applied to the sample for a certain period of time to drive back K ions to negative electrode. The measured remnant voltage became negative. Then positive bias voltage +2 V was applied and the current was measured as shown in blue line in Figure 5(c). The starting current was 24.7 nA, lower than the starting current (29.5 nA) in black curve. Figure 5(b) describes the process shown in blue curve in Figure 5(c). Due to the negative bias voltage applied,

accumulated K ions near negative terminal induce a negative remnant voltage which cancels part of electric potential when positive bias voltage was applied. Thus, the starting current is lower than the value obtained with no prior applied voltage. If larger amplitude of negative bias voltage is applied, lower starting current can be then measured due to increased ion accumulation near negative electrode. In the first 10 s, the current increases more sharply from 24.7 nA to 29.8 nA (blue curve) than from 29.5 nA to 32.6 nA (black curve). It is consistent with the observation discussed above that greater amount of K ions moves in the same duration under same bias voltage when accumulated K ions are driven back. After 300 s, although the blue curve tends to close to the black curve, there is still a gap of approximately 2.5 nA between them. It is possible that when K ions are scattered by electrons, some of them hop to the oxygen vacancies in the nearby channels where the current density is low due to the high oxidation state of surrounding Mo atoms. It makes these K ions hard to be driven back by electron wind force. Consequently, longer duration is required (blue curve) to achieve equilibrium. This is also the reason we could still detect accumulated K ions by the EDX measurement half an hour after K ions packing.

III. CONCLUSION

In summary, we report an interesting observation of reversible electromigration of intercalated K ions in layered single crystalline $K_x\text{MoO}_3$ nanobundles. The varied concentration distribution of K ions from the EDX measurement, the remnant voltage measurement, and I-t measurement confirms the observation that when subjected to the application of electric current, K ions in the lattice migrate along nanobundle, and ions move in parallel to the flowing direction of electrons. Our results reveal that K ions are driven by electron wind force. Upon the reversal of current, accumulated K ions near one electrode are driven back and gather near the opposite electrode. For the rapid diffusion of K ions in the lattice, the duration required to induce significant accumulation of K ions and the relaxation time are significantly

shorter than the value reported in other interstitial systems. The layered structure is preserved during reversible electromigration of intercalated ions with no expansion, void or cracks observed.

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- ¹D. G. Pierce and P. G. Brusius, *Microelectron. Reliab.* **37**, 1053 (1997).
- ²R. S. Sorbello, *Solid State Phys.* **51**, 159 (1997).
- ³P. S. Ho and T. Kwok, *Rep. Prog. Phys.* **52**, 301 (1989).
- ⁴J. van Ek and A. Lodder, *J. Phys.: Condens. Matter* **3**, 7331 (1991).
- ⁵J. van Ek and A. Lodder, *J. Phys.: Condens. Matter* **3**, 8403 (1991).
- ⁶J. R. Lloyd, *Semicond. Sci. Technol.* **12**, 1177 (1997).
- ⁷B. C. Regan, S. Aloni, R. O. Ritchie, U. Dahmen, and A. Zettl, *Nature* **428**, 924 (2004).
- ⁸M. A. Haase, J. M. DePuydt, H. Cheng, and J. E. Potts, *Appl. Phys. Lett.* **58**, 1173 (1991).
- ⁹J. R. Lloyd, M. R. Polcari, and G. A. Mackenzie, *Appl. Phys. Lett.* **36**, 428 (1980).
- ¹⁰H. Ohtsuka and Y. Sakurai, *Solid State Ion.* **144**, 59 (2001).
- ¹¹L. Zhou, L. Yang, P. Yuan, J. Zou, Y. Wu, and C. Yu, *J. Phys. Chem. C* **114**, 21868 (2010).
- ¹²A. M. Hashem, M. H. Askar, M. Winter, J. H. Albering, and J. O. Besenhard, *Ionics* **13**, 3 (2007).
- ¹³L. Mai, B. Hu, W. Chen, Y. Qi, C. Lao, R. Yang, Y. Dai, and Z. L. Wang, *Adv. Mater.* **19**, 3712 (2007).
- ¹⁴J. Graham and A. D. Wadsley, *Acta Crystallogr.* **20**, 93 (1966).
- ¹⁵Z. Hu, C. Zhou, M. Zheng, J. Lu, B. Varghese, H. Cheng, and C.-H. Sow, *J. Phys. Chem. C* **116**, 3962 (2012).
- ¹⁶J. Garcia-Barriocanal, A. Rivera-Calzada, M. Varela, Z. Sefrioui, E. Iborra, C. Leon, S. J. Pennycook, and J. Santamaria, *Science* **321**, 676 (2008).
- ¹⁷T. Ishihara, H. Matsuda, and Y. Takita, *J. Am. Chem. Soc.* **116**, 3801 (1994).
- ¹⁸H. Nakajima, M. Yoshioka, and M. Koiwa, *Acta Metall.* **35**, 2731 (1987).
- ¹⁹R. C. Brouwer and R. Griessen, *Phys. Rev. Lett.* **62**, 1760 (1989).
- ²⁰A. Priemuth, *Phys. Status Solidi A* **67**, 505 (1981).
- ²¹I. A. Blech and E. S. Meieran, *J. Appl. Phys.* **40**, 485 (1969).
- ²²M. W. Lane, E. G. Liniger, and J. R. Lloyd, *J. Appl. Phys.* **93**, 1417 (2003).
- ²³J. R. Lloyd and J. J. Clementi, *Thin Solid Films* **262**, 135 (1995).