Operando Surface Science Methodology Reveals Surface Effect in Charge Storage Electrodes

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ABSTRACT

Surface and interface play critical roles in energy storage devices, calling for operando characterization techniques to probe the electrified surfaces/interfaces. In this work, surface science methodology including electron spectroscopy and scanning probe microscopy has been successfully applied to visualize electrochemical processes at operating electrode surfaces in an Al/graphite model battery. Intercalation of anions together with cations is directly observed in surface region of the graphite electrode with tens of nanometers thickness, whose concentration is amazingly one
order higher than that in bulk. An intercalation pseudocapacitance mechanism and a
double specific capacity in the electrode surface region are expected based on the
super-dense intercalants and anion/cation co-intercalation, which are in sharp contrast
with the battery-like mechanism in the electrode bulk. The distinct electrochemical
mechanism at electrode surface is well verified by performance tests of real battery
devices, showing that surface-dominant nanometer thick graphite cathode
outperforms bulk-dominant micrometer thick graphite cathode. Our findings highlight
the important surface effect of working electrodes in charge storage systems.

**Keywords:** surface science methodology, aluminum ion battery, operando
characterization, surface effect

**INTRODUCTION**

Fundamental understanding of elementary electrochemical processes at electrified
surfaces/interfaces of electrochemical energy storage devices strongly relies on
development and application of in-situ/operando characterization techniques.
Significant progresses have been made in past decades [1, 2], and successful
characterization techniques include X-ray diffraction (XRD) [3-5], transmission
electron microscopy (TEM) [6-9], X-ray spectroscopy and topography [4, 10, 11],
nuclear magnetic resonance (NMR) [12], etc. Rich electronic, chemical, and
geometric information from the bulk regions of electrodes and electrolytes can be
derived while overlooking surface and interface processes. It is well known that
device performance is mainly governed by surface and interface
electrochemical reactions in most state-of-art nanosized electrodes [10, 13, 14],
which thus call for operando surface and interface analysis.

Surface science methodology such as electron spectroscopy and scanning probe
microscopy has proven to be successful in providing a detailed description of how
chemical reactions take place on solid surfaces [15]. Applications of the sophisticated
surface science techniques to electrochemical devices should well address key issues
at the electrified surface/interface, which however remain less explored and more
challenges in contrast with the surface catalysis research [15-18]. First, surface science analysis is mostly done in ultrahigh vacuum (UHV) and thus difficult to explore electrochemical reactions occurring at liquid/solid interfaces. Nevertheless, solid-state or ionic liquid (IL) electrolytes are UHV compatible [6, 7, 9, 10, 19, 20] and even water/solid interfaces can be probed by newly developed near ambient pressure surface techniques [18, 21, 22]. Second, most surface-sensitive techniques need to probe open and well-defined surfaces while electrode surfaces in real electrochemical devices are all buried by electrolytes and current collectors which are totally inaccessible to surface probes. Thus, it is crucial to construct model electrochemical devices having planar and open electrified surfaces for surface analysis [9, 10, 19, 23].

In this work, taking an aluminum (Al) ion battery (AIB) as an example [24, 25], we build planar Al/graphite model battery consisting of Al foil anode | 1-ethyl-3-methylimidazolium chloride (EMImCl)/AlCl$_3$ (1:1.3 by mole ratio) IL electrolyte | highly ordered pyrolytic graphite (HOPG) cathode. Using the UHV compatible IL electrolyte and open electrode, the model devices have been successfully placed into various surface systems including Raman, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) for multiple operando characterizations of the working electrode surfaces. The comprehensive surface analysis provides an unprecedented chance to follow elementary electrochemical reaction steps at electrode surfaces. More interestingly, a distinct electrochemical reaction mechanism has been identified in the surface regions of a bulk electrode, which enables us to successfully predict doubling of the specific capacity by using surface-dominant nanometer-thick graphite electrode materials in the real coin-type batteries.

RESULTS AND DISCUSSION

Model AIB devices and their electrochemical behaviors

For the operando surface science analysis, a planar model AIB with open electrode
surface has been designed. As illustrated in Fig. 1a (left), a freshly exfoliated HOPG flake (a few millimeters long and wide, and tens of micrometers thick) was employed as the working electrode (WE) which was parallelly placed with an aluminum foil (counter electrode, CE). IL electrolyte was dropped on the gap between them. Notably, most part of the HOPG surface was free from the electrolyte and open for the surface probe. Alternatively, HOPG flake, glass fiber separator filled with IL electrolyte, and Al foil can be stacked to form a sandwich-like AIB model device (Supplementary Fig. 1a). Electrochemical tests were performed over the model devices. As shown in Fig. 1b and Supplementary Fig. 1b, the intercalation peaks around ~1.9, 2.1, and 2.4 V were observed in cyclic voltammetry (CV) curves upon charging the model devices. Furthermore, galvanostatic charge-discharge (GCD) curves of the model batteries are shown in Fig. 1c, and two charged plateaus in the range of 1.9 – 2.3 V and 2.3 – 2.4 V are clearly found. Overall, the model devices display the same electrochemical behaviors as the real Al/graphite batteries [24].

In addition to the electrochemical performance, diffusion of ions inside HOPG electrode was recorded in real-time by optical microscope (OM) using an operando OM/Raman cell equipped with a transparent quartz window (Supplementary Fig. 2). Fig. 1d displays a set of images captured at 2 V for different charging times. It can be seen that dark contrast of the graphite surface is induced by the ion intercalation and the diffusion frontiers can be clearly distinguished by OM. Accordingly, ultrafast (~3.7 μm/s) and ultralong (up to centimeters) diffusion of the intercalated ions underneath the HOPG surface has been directly confirmed through the operando OM measurements. The varied optical contrasts suggest the different charging states (Supplementary Fig. 3, Videos 1 - 3). Based on open HOPG electrode and long-distance lateral ion transport within the electrode, our planar model battery with the HOPG WE provides an ideal model system for the operando surface science studies (Fig. 1a right).

**Operando surface science analysis of the graphite electrode**

Structural changes of the graphite electrode were studied by operando Raman
spectroscopy at the open electrode surface of the planar AIB device (Fig. 2a). Upon charging, the characteristic G band of pristine graphite (denoted as \(G_{uc}\), uncharged state) shifts to higher wavenumber positions, which can be assigned to graphene layers charged by adjacent ions \(G_c\) [26]. Charging at 2.2 V produces a stage-2 graphite intercalation compound (GIC) as indicated by the dominant \(G_{c1}\) peak at \(~1620\) cm\(^{-1}\). With the potential set at 2.35 V, a new peak around 1635 cm\(^{-1}\) (denoted as \(G_{c2}\)) appears and finally becomes dominant, which can be attributed to more strongly charged graphene layers in stage-1 GIC [27-30]. Besides the graphite signals, intercalated electrolyte species have also been detected by Raman from the open electrode surface. When the potential is higher than 2.1 V, two peaks at \(~350\) and \(~600\) cm\(^{-1}\) start to appear (Fig. 2a), which are characteristic for \(\text{AlCl}_4^-\) and EMI\(^+\) ions, respectively [24]. Therefore, operando Raman measurements give direct evidence of co-intercalation of \(\text{AlCl}_4^-\) and EMI\(^+\) ions and formation of stage-1 GIC in the surface region of HOPG which depth is less than 100 nm due to strong absorption of light by graphite [31]. Upon the discharging, the evolution of G band is fully reversible, i.e. \(G_{c2} \rightarrow G_{c1} + G_{c2} \rightarrow G_{c1} \rightarrow G_{uc} + G_{c1} \rightarrow G_{uc}\), when probing the HOPG surface close to the electrolyte/graphite interface (Supplementary Fig. 4).

The sandwich-like AIB devices (Supplementary Fig. 1) have been loaded into a system for operando XPS measurements. Chemical component and charge transfer in surface region of the graphite electrode were investigated in detail. During the XPS measurements graphite electrodes were always grounded and external potentials ramped from 1.95 to 2.45 V \((V_{\text{graphite}} - V_{\text{Al}})\) were applied to Al anodes (Supplementary Fig. 1). During the charging process, Al 2p, Cl 2p, and N 1s core-level signals appear at lower binding energy (BE) positions and show remarkable intensity increase (Fig. 2b and details in Supplementary Figs. 5-7). These newly appeared spectra all present -1.7 eV BE shifts compared with those from the supported IL overlayers (Supplementary Fig. 8 and Table 1). In contrast, the C 1s signal intensity decreases largely due to attenuation by the intercalated ions (Fig. 2c and Supplementary Fig. 9). A HOPG electrode has been deliberately coated by ultrathin gold layer and Au 4f peak position acquired from this operating electrode always remains constant during the
charging process (Supplementary Fig. 10). This reference experiment confirms that the newly appeared Al 2p, Cl 2p, and N 1s signals are caused by electrochemical intercalation of electrolyte ions into HOPG. Work function of the operating HOPG electrode surface has been measured by operando scanning Kelvin probe microscopy (SKPM), which increases by \( \sim 1.7 \) eV in the fully charged state (Supplementary Fig 11). Thus, it is the downshift of the Fermi level at the charged graphite surface that results in the observed rigid BE shifts for all intercalated Al, Cl, N, and C elements [32] (Supplementary Fig. 12).

The chemical composition of the intercalants and GICs can be further determined from the XPS data (Fig. 2d and e). The intercalation of \( \text{AlCl}_4^- \) together with EMI\(^+\) is unambiguously confirmed by the facts of \( \text{Al}_{\text{int}}/\text{Cl}_{\text{int}} = 1: 4.1 \) and \( \text{Al}_{\text{int}}/\text{N}_{\text{int}} = 1:1.6 \) which agrees with the above operando Raman results. By subtracting the contributions from guest C atoms in intercalated EMI\(^+\) (C-N at 285.2 eV/(C-N)\(_{\text{int}}\) and C-C at 283.6 eV/(C-C)\(_{\text{int}}\)) [20, 33], the atomic ratios between \( \text{Al}_{\text{int}} \) and \( \text{C}_{\text{host}} \) atoms (\( \text{C}_{\text{host}} \) including uncharged graphite at 284.5 eV/C\(_{\text{uc}}\) and charged graphite at 283.9 eV/C\(_{\text{c}}\), Fig. 2c and Supplementary Fig. 13) at different potentials are obtained (Fig. 2e). We find that the \( \text{Al}_{\text{int}}/\text{C}_{\text{host}} \) ratio has increased to 1:1.7 at the fully charged state, which is about one order higher than the theoretical limit in AIB (1:24) [5]. For the first time, the electrochemical reaction of AIB in the surface region can be described by the following formula:

\[
\text{C}_n + 5[\text{AlCl}_4^-] + 4[\text{EMI}^+] \rightarrow \text{C}_n[\text{AlCl}_4]_5[\text{EMI}]_4 + e^- \quad (n \sim 8.5). \quad (1)
\]

The small \( n \) (8.5) indicates an abnormal super-dense intercalant state, forming multi-layered cations/anions within the graphene layers like the formation of the super-dense lithium phase in bilayer graphene [9, 34].

Such super-dense intercalation structure and large amount of cations co-intercalation may be unstable, and the electronic structure evolution induced by redistribution of the intercalated cations and anions under open circuit (OC) condition can be investigated by operando XPS. The Al, Cl ad N core levels shift by +0.4 eV at the OC state for 72 h (Supplementary Fig. 14). Such relaxation may be attributed to
charge redistribution in the cation/anion multilayers in between the graphite layers similar as in supercapacitors [35], which however does not happen in the bulk regions (Supplementary Fig. 15).

**Distinct electrochemical process at electrode surface compared to bulk**

In order to make a comparison of the electrochemistry at electrode surface and in bulk, quasi in-situ Raman and XPS measurements were carried out on a fully charged electrode subjected to mechanical exfoliation (exposure of the bulk region to surface analysis) (Supplementary Scheme 1). Figure 3a shows depth-dependent graphite intercalation structures: stage-1 GIC at the surface vs. stage-4 GIC in the bulk. Our experimental evidence for different intercalation stages between the electrode surface and bulk confirms the theoretical hypothesis of core-shell structure of intercalated electrode particles [30]. XPS Al 2p, N 1s, and C 1s (C-N) peaks from the bulk region have similar BE positions as those from the as-charged surface but their intensities are all strongly weakened (Fig. 3b and Supplementary Fig. 16), while the C 1s signal from C\textsubscript{host} atoms becomes much stronger (Supplementary Fig. 16). The determined $\text{Al}_{\text{int}}/\text{C}_{\text{host}}$ ratio is 1:19.1 and $\text{Al}_{\text{int}}/\text{N}_{\text{int}}$ ratio is 1:0.7 (Fig. 2e and Supplementary Fig. 16). Both intercalated $\text{AlCl}_4^-$ and co-intercalated EMI$^+$ concentrations in bulk are much smaller than those in surface. To validate the semi-quantitative results from the XPS analysis, the chemical composition of the fully charged graphite electrode was analyzed by chemical analysis methods producing the similar results. Fig. 2e and Supplementary Fig. 16 indicate $\text{Al}_{\text{int}}/\text{C}_{\text{host}} = 1: 17.5$ and $\text{Al}_{\text{int}}/\text{N}_{\text{int}} = 1:1.1$, which are considered to be normal in comparison with previous reports [5, 25]. The depth-dependent intercalation reaction can be also confirmed by ex-situ time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements. The mass spectrometry (MS) signals related to the intercalation concentration ($\text{Al}/\text{C}_3$) keep on decreasing with the increasing sputtering time (Supplementary Fig. 17), revealing that the intercalant concentration gradient is present in the surface region. The thickness ($d$) of the unusual surface region is estimated to be within 100 nm (Supplementary Fig. 18).
The distinct electrochemical behavior in the surface region is further verified by operando XRD measurements (Supplementary Fig. 19) over two kinds of graphite materials: nanometer thick graphite films \((d = \sim 50 \text{ nm})\) vs. micrometer thick graphite films \((d = \sim 20 \text{ μm})\). An ordered stage-4 GIC structure forms in the thick graphite film electrode (Fig. 3c), while the fully charged ultrathin graphite film electrode has a disordered structure (Fig. 3d). Ex-situ grazing incidence X-ray diffraction (GIXRD) measurement probes the surface region directly and confirms the same surface structure (Supplementary Fig. 20). The volume expansion of ultrathin electrode during intercalation was measured by in-situ AFM analysis over a 52 nm thick graphite flake which reveals more than 5-fold volume expansion (Fig. 3e and f, Supplementary Figs. 21 and 22). The micrometer thick graphite flake shows the normal 2-fold thickness increase by imaging its cross section with ex-situ scanning electron microscopy (Fig. 3g and 3h). The much larger volume expansion and less-ordered phase in the nanometer thick cathode is consistent with the above finding of super-dense intercalated multi-layered ions in graphite layers at the surface region as concluded from the operando XPS measurements (Fig. 2e).

**Electrode surface effect on battery performance**

The above characterization results demonstrate a remarkable surface effect on the electrochemical reaction in AIB, which may subsequently affect the device performance. We first explored the intercalation kinetics in electrodes of nanometer thick graphite film \((d = \sim 50 \text{ nm}, \text{ area of } 1 \times 1 \text{ cm}^2)\) and micrometer thick graphite film \((d = \sim 20 \text{ μm}, \text{ area of } 1 \times 1 \text{ cm}^2)\), in which surface region and bulk region are dominant in the two electrodes, respectively. CV tests are performed at different scan rates in the three-electrode mode. According to Fick’s law of semi-infinite diffusion, peak current \((i)\) and scan rate \((v)\) follow the formula of \(i = a \cdot v^b\) [36]. Much sharper redox peaks at lower intercalation potential were observed in the CV curves acquired from the device using the ultrathin graphite film cathode (Fig. 4a and Supplementary Fig. 23) with a derived \(b\) value of \(\sim 0.91\) (Fig. 4b), revealing a charge-transfer-limited intercalation pseudocapacitance process [37]. In contrast, the \(b\) value measured from the device...
using the thick graphite film cathode is 0.57, indicating a diffusion-limited battery-like process. The two contrast charging mechanisms are also present in the real coin-type devices (Supplementary Fig. 24). The sharper CV peaks observed from the nanometer thick graphite electrodes also reveal the higher diffusion rate of intercalated ions within the ultrathin electrodes and the formed uniform local structure around the intercalated ions [14].

The above characterization data confirm that electrochemical processes within electrode surface regions or in ultrathin electrodes are dominated by the intercalation pseudo-capacitance charging mechanism as manifested by one order higher $\text{AlCl}_4^-$ concentration compared with the theoretical value but co-intercalation of $[\text{AlCl}_4^-]_3$ and $[\text{EMI}^+]_4$. Accordingly, the theoretical capacity is expected to be doubled in this case. Guided by this insight, we assembled two coin-type devices using nano graphite powder (NGP) (3-10 nm thick and 5-10 μm large) and micrometer graphite powder (MGP) (diameter ~15 μm) as cathode materials, respectively. As shown in Fig. 4c the capacity has been improved from 61 mAh·g$^{-1}$ with the MGP cathode to 116 mAh·g$^{-1}$ with the NGP cathode at 0.5 A·g$^{-1}$, and such performances are maintained for 100 cycles (Supplementary Fig. 25a) and at higher current density (Supplementary Fig. 25b). Notably, the diffusion length in both NGP and MGP cathodes are in the same scale of micrometers (Supplementary Fig. 26) and the only difference is the thickness. As shown above (Fig. 1d), intercalation of electrolyte ions and their lateral diffusion in graphite cathodes are feasible and ultrafast in the Al/graphite battery [24, 25]. Therefore, the observed different electrochemical reaction mechanisms and device performances between the surface and bulk regions should not be attributed to the diffusion limit or surface adsorption, which are commonly used to explain size effect in energy storage processes [14, 38, 39]. It is suggested that the demonstrated surface effect may originate from the enhanced structural flexibility of the electrode surface regions [40] allowing to accommodate more intercalation ions in graphene layers (Fig. 4d) and explains the origin of better performance with the nanometer-thick graphene electrodes compared with the micrometer-thick graphite electrodes [25, 41].
CONCLUSION

The distinct electrochemical intercalation reactions in the electrode surface regions were revealed by comprehensive operando surface science measurements over well-designed Al/graphite model batteries. Multi-layer super-dense anions with co-intercalated cations whose concentration is about one order higher than that in electrode bulk were observed. The depth-dependent charge storage mechanism can be described as the intercalation pseudo-capacitance mechanism dominant in the surface regions in contrast with the battery-like process occurring in the bulk regions. The revealed surface effect on electrochemical storage guides to double the capacity by using the nanometer thickness graphite electrode. This work suggests a new strategy for operando studies of surface electrochemical reaction over electrode surface using surface-sensitive techniques and highlights the significance of electrode surfaces in electrochemical device performances.

METHODS

Operando Raman and XPS measurements

Operando Raman characterizations were based on the planar model batteries. The model batteries were placed into an in-situ Raman cell (Supplementary Fig. 2). The battery devices and then the cell were assembled in an Ar-filled glove box (H_2O, O_2 < 0.5 ppm). Raman spectra were recorded with a LabRAM HR 800 Raman spectrometer using a 532 nm laser. The incident laser was illuminating on the open area of the HOPG flake.

The model battery used for XPS measurements is in sandwich structure (Supplementary Fig. 1) which was assembled onto Omicron-type direct-current heating sample holders in glove box and then transferred to the XPS analysis system by using a mobile UHV transfer chamber. The HOPG flake (5 × 12 mm^2) was connected with the sample holder and thus grounded. A small piece of glass fiber separator layer adsorbed with IL was placed on one end of the HOPG flake.
Subsequently, a small piece of Al foil was put on the top of the separator and then connected with a contact bar which were insulated from the sample holder.

XPS core level spectra were recorded under UHV conditions \( (p < 10^{-8} \text{ mbar}) \) using pass energy of 20 eV. Data analysis was done by Casa-XPS software with a Shirley background and 70/30 Gaussian-Lorentzian fits. The chemical composition (Fig. 2d and e) of the GICs is determined by XPS fitting results (as shown in Supplementary Fig. 13). \( \frac{\text{Al}_{\text{int}}}{\text{C}_{\text{host}}} \) is calculated by the formula: \( \frac{\text{Al}_{\text{int}}}{\text{C}_{\text{host}}} = \frac{\text{Al}_{\text{int}}}{(\text{C}_{\text{total}} - \text{N}_{\text{int}} \times 3)} \) according to the stoichiometric ratio of EMI$^+$. 

The comparison between surface and bulk were measured by quasi in-situ XPS and Raman measurements on exfoliated as-charged HOPG electrodes (Supplementary Scheme 1). For each process including assembling, transfer, charging and exfoliation, exposure to air has been avoided in both operando and quasi in situ measurements.

**In-situ AFM measurements**

In-situ AFM was performed over a thin graphene nanosheet (mechanical exfoliation from a HOPG crystal) on a flat glassy carbon (GC) substrate (Gaoss Union company Wuhan, China) operated by a Cypher ES AFM (Asylum Research, Oxford Instruments, USA) installed in an Ar-filled glove box (Supplementary Fig. 21). Before testing, the sample is calcined under Ar at 900 ℃ for 3 h to remove the residue tape. AFM tip (AC160TSA-R3-10, 250 Hz, 20 N/m) is totally immerged in the electrolyte drop and can measure the nanosheet height during the charging. For comparison, the expansion of thick graphite flake was measured by ex-situ SEM (Phenom ProX, Phenom World, Netherlands) imaging of the cross section over the same sample edge.

**Operando XRD measurements**

Large area high-quality graphene films with different thickness (Supplementary Fig. 23) were synthesized by high temperature thermo-reduction of graphene oxide (GO) layers [25, 42]. Operando XRD measurements of the graphene and graphite electrodes were studied by a Rigaku Ultima IV X-ray diffractometer (Cu Ka, 40 kV, 40 mA) in an in-situ XRD cell (Supplementary Fig. 19). The electrochemical operando XRD patterns were acquired in 2θ range of 15° - 35° with a scan rate of 5°·min$^{-1}$. Operando
XRD analysis was performed using constant charging potential as illustrated in Fig. 3c and d. The stage number n of the GIC is calculated by the ratio between two interplanar spacing of dominate diffraction peaks: (0, 0, n+1) and (0, 0, n+2) [43]. Ex-situ GIXRD measurements were performed by SmartLab XRD (Rigaku, Japan). The angle of incidence X-Ray is 1° and 0.3° (Supplementary Fig. 20). The operando GIXRD patterns were acquired in 2θ range of 20° - 30° with a scan rate of 5°·min⁻¹.

SUPPLEMENTAL DATA
Supplementary data are available at NSR online.

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AUTHOR CONTRIBUTIONS
Q.F. conceived and guided the project. C.W. carried out surface science investigations in model devices. Y.N., S.L, C.X., and Y.L. performed part of surface science studies in model devices. H.H., Z.W., S.G., and C.W. carried out performance tests over real coin-type batteries. Q.C. and L.C. assisted in operando SKPM measurements. L.P.
and C.G. provided the ultrathin graphite materials. X.L. assisted in operando XRD measurements. All authors contributed to interpreting the data and writing the manuscript.

**Conflict of interest statement.** None declared.

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Figure 1. Model AlB devices and their electrochemical behaviors. (a) Schematic for Al/graphite model battery enabling simultaneous electrochemical measurements and surface science measurements using photons or scanning probes over the open electrodes (left panel); Side views of the model battery showing that ions intercalate into graphene layers from liquid/graphite interfaces and diffuse over $\mu$m or even mm distances (right panel). (b) Cyclic voltammetry (CV) curves (0 - 2.45 V, 0.5 mV/s) and (c) Galvanostatic charge-discharge (GCD) curves (60 $\mu$A, cut off voltage: 2.42 V, discharge plateaus: $\sim$2.2 V) from the model battery. (d) Operando OM images ($700 \mu$m x $950 \mu$m) captured at the indicated charging times on 2V over HOPG electrode. Diffusion frontiers are highlighted by red dash lines.
Figure 2. Operando surface science analysis of the graphite electrode. (a) Operando Raman spectra showing evolution of graphite G band (left) and intercalation ions signals (middle) upon charging at different potentials and different times (right). (b and c) A set of operando XPS Al 2p (b) and C 1s (c) spectra when charging from 1.95 to 2.45 V. The bottom Al 2p spectrum in (b) is from surface-adsorbed $\text{AlCl}_4^-$ species ($\text{Al}_{\text{ads}}$) contaminated on the pristine electrode at open circuit voltage (OCV), while the top spectrum in (b) is mainly from intercalated $\text{AlCl}_4^-$ species ($\text{Al}_{\text{int}}$) on the completely charged electrode (2.45 V for 2 h). The bottom and top C 1s spectra in (c) are from the electrode surface before and after the charging process, respectively. (d) Dependence of intercalated Cl ($\text{Cl}_{\text{int}}$) and intercalated N ($\text{N}_{\text{int}}$) contents with intercalated Al ($\text{Al}_{\text{int}}$) contents in the charging process, showing that Cl/Al and N/Al atomic ratios are 4.1 and 1.6 at all potentials. (e) Atomic ratios between intercalated Al ($\text{Al}_{\text{int}}$) and host-C ($\text{C}_{\text{host}}$) at different potentials. Al/C$_{\text{host}}$ ratios at the fully charged state from the theory limit (dash line)$^{[5]}$, XPS measurement over the bulk electrode (red star), and chemical analysis of the whole graphite electrode (green star) are included (Supplementary Fig. 16).
Figure 3. Depth/thickness-dependent electrochemical intercalation process. Distinct electrochemical intercalation process at surface region. (a and b) Raman spectra (a) and XPS Al 2p spectra (b) acquired from as-charged graphite surface and bulk region of the electrode after exfoliation of the surface layer, respectively. (c and d) Operando XRD patterns from (c) thick graphite film ($d = \sim 20 \, \mu m$) electrode and (d) thin graphite film ($d = \sim 50 \, nm$) electrode. The bottom and top XRD patterns in (c) and (d) are from the electrode before and after the charging process, respectively. (e and f) In-situ atomic force microscope (AFM) images of a graphene nanosheet at OCV (E) and fully charged state (f), respectively. The inset line profiles show the step heights labelled by the red rectangles. (g and h) Ex-situ SEM cross-section images of a graphite flake at OCV (g) and fully charged state (h), respectively.
Figure 4. Surface/thickness effect on battery performance. (a) CV curves of the electrochemical devices based on thick graphite film ($d \approx 20 \mu m$) and ultrathin graphite film ($d \approx 50$ nm) electrodes (scan rate: 0.5 mV/s) in the three-electrode mode. (b) Dependence of peak current ($i$) on the scan rate ($v$) and the derived slopes ($b$) of $\log(i)/\log(v)$ lines for the 1$^{st}$ intercalation peak around 1.9 V, marked by arrows in (a). (c) GCD curves of real AlB devices after 20$^{th}$ cycle at a current density of 0.5 A/g using nano graphite powder (NGP) and micrometer graphite powder (MGP) as cathode materials (cut off voltage: 2.42 V). (d) Schematic illustration of depth-dependent charge storage processes: multi-layer $\text{AlCl}_4^-$ and $\text{EMI}^+$ intercalated in near surface region with intercalation pseudo-capacitance mechanism vs. dominant $\text{AlCl}_4^-$ intercalation in bulk region with battery process.