

Chao Wang<sup>1,2</sup>

Qiang Fu<sup>1</sup> and Xinhe Bao<sup>1,3</sup>

<sup>1</sup>State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China

<sup>2</sup>University of Chinese Academy of Sciences, Beijing 100049, China

<sup>3</sup>University of Science and Technology of China, Hefei 230026, China

Chao0354@dicp.ac.cn

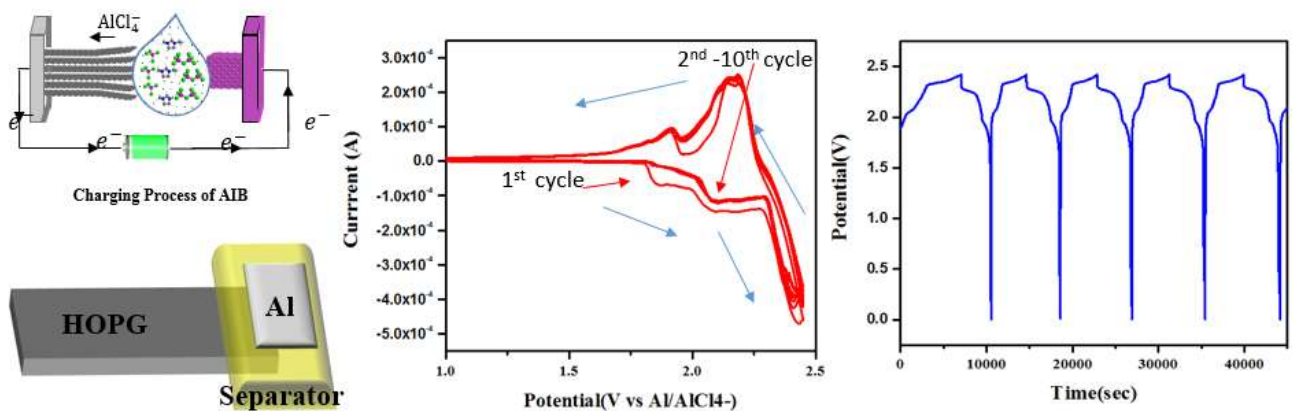
## In-situ investigations of the rechargeable aluminum ion battery by XPS, Raman and optical microscope

Rechargeable aluminum ion battery is one of the most promising energy storage device owing to crustal abundance, high theoretical power density and excellent safety [1]. In 2015, Dai's group developed a novel aluminum ion battery (AIB) consisting graphitic foam cathode, aluminum anode, and  $\text{AlCl}_3$ /1-ethyl-3-methylimidazolium chloride (EMIC) ionic liquid (IL) electrolyte exhibited ultrafast rechargeable rate and excellent cycle stability [2]. However, the fundamental science problems of AIB have been rarely studied by researchers. Herein, we built a model battery consisting highly oriented pyrolytic graphite (HOPG) cathode, Al foil anode and  $\text{AlCl}_3$ /EMIC IL electrolyte. The same electrochemistry performance as the real ones such that the in-situ studies using Raman, XPS, and optical microscope can be performed with the model battery. By designing the transfer chamber and sample holder, in-situ XPS investigated of the electrochemical intercalation process of chloroaluminate anion-graphite system has been achieved for the first time. Except for XPS Al and Cl signals, we also observed the increase of N1s signal. We believe that there exists the co-intercalation of  $\text{EMI}^+$  and  $\text{AlCl}_4^-$ , which has been further proved by in-situ Raman. By analyzing the binding energy, the electronic structure (work function, charge transfer) change of the graphite cathode has been revealed during the intercalation process. Furthermore, the in-situ observation of the HOPG during charging and discharging process via optical microscope could provide some intuitive information such as the diffusion of ions, color and macrostructure change of HOPG.

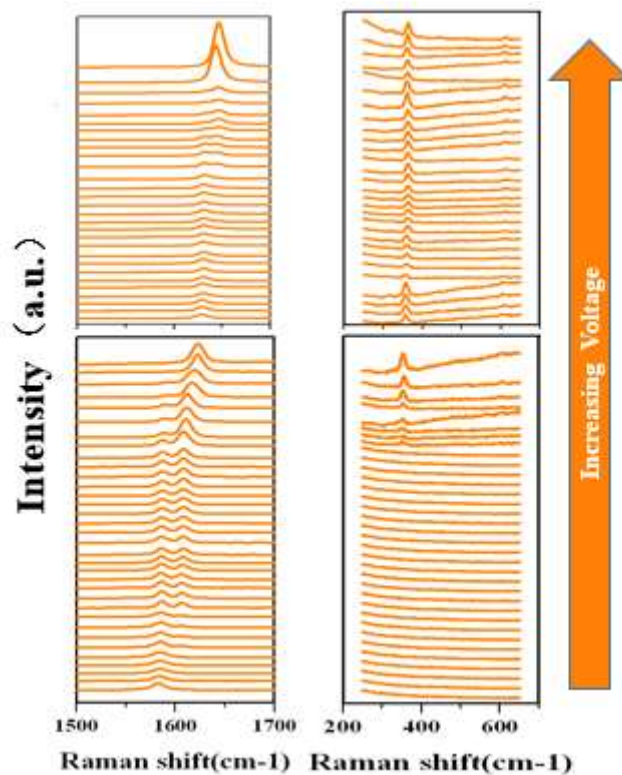
### References

- [1] Li, Q. & Bjerrum, N. J et al J. Power Sources 110, (2002) 1–10.
- [2] Lin M C, Dai H J et al Nature 520 (2015) 325-328

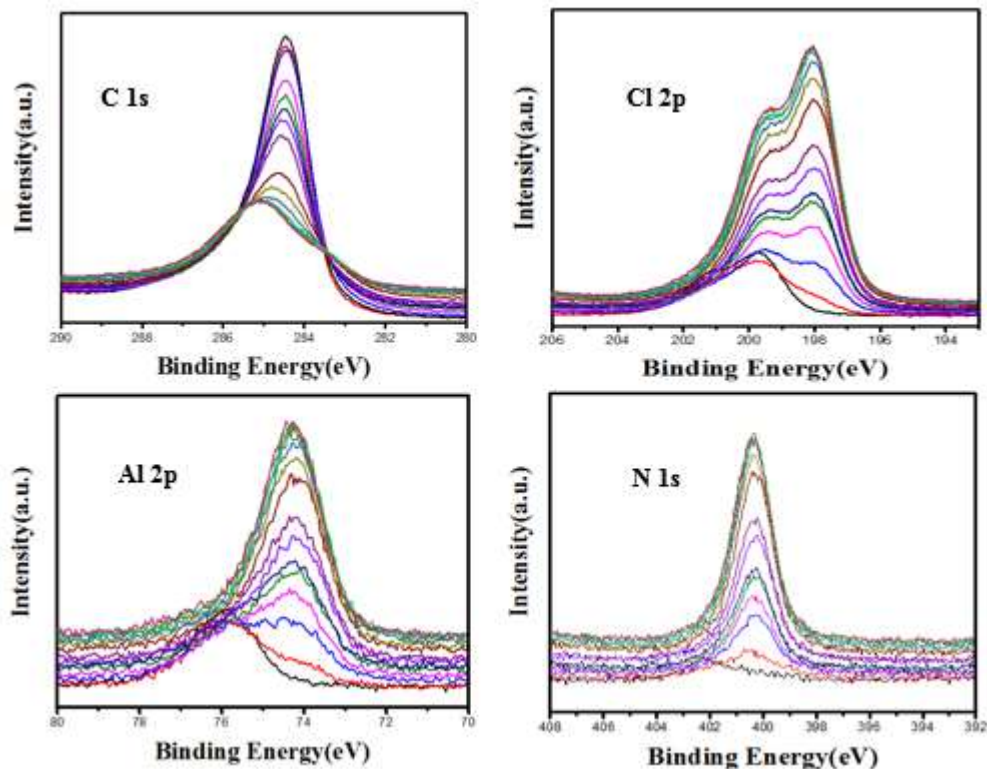
### Figures



**Figure 1:** Left: the schematic diagram of the Al|EMIC- $\text{AlCl}_3$  (1:1.3 by mole) |HOPG model battery, notice that only one end of HOPG is submerged by electrolyte. Middle and right: CV curve (scan rate is 0.5mV/s) and the voltage profile of first five cycles, which exhibit the same performance with the real ones [2].



**Figure 2:** In-situ Raman spectra of the uncovered part of the HOPG electrode during charging process. Except for the typical change of the G band, the  $\text{AlCl}_4^-$  ( $\sim 350\text{cm}^{-1}$ ) and  $\text{EMI}^+$  ( $\sim 600\text{cm}^{-1}$ ) have also been detected.



**Figure 3:** Similarly with the in-situ Raman, in-situ XPS spectra was collected from the uncovered part of HOPG electrode during charging process. As expected, the intensity of Al 2p and Cl 2p would increase because of the intercalation and the C 1s decrease because of the expansion. Furthermore, we also found the increase of N 1s signal. Combined with the Raman spectra, we assumed that there exist the co-intercalation of  $\text{AlCl}_4^-$  and  $\text{EMI}^+$ .