

Al Batteries Activated at Low Temperature

A remarkable life > 20,000 cycles at rate 6C (charge duration 10 min) was achieved for an Al battery operating at low temperatures, corresponding to a battery life > 50 years if charged or discharged once daily.

Among various battery techniques, the aluminum-ion battery has gained attention because of the great abundance, low cost and high safety of aluminum (Al). A rechargeable aluminum-ion battery (AIB) system based on reversible reduction and oxidation of aluminum at the Al negative electrode

and reversible intercalation or deintercalation of chloroaluminate anions at the graphite positive electrode has been intensively developed. Various ionic liquids are known to exhibit melting points well below 0 °C, which could be utilized to facilitate operation of the battery in cold conditions.

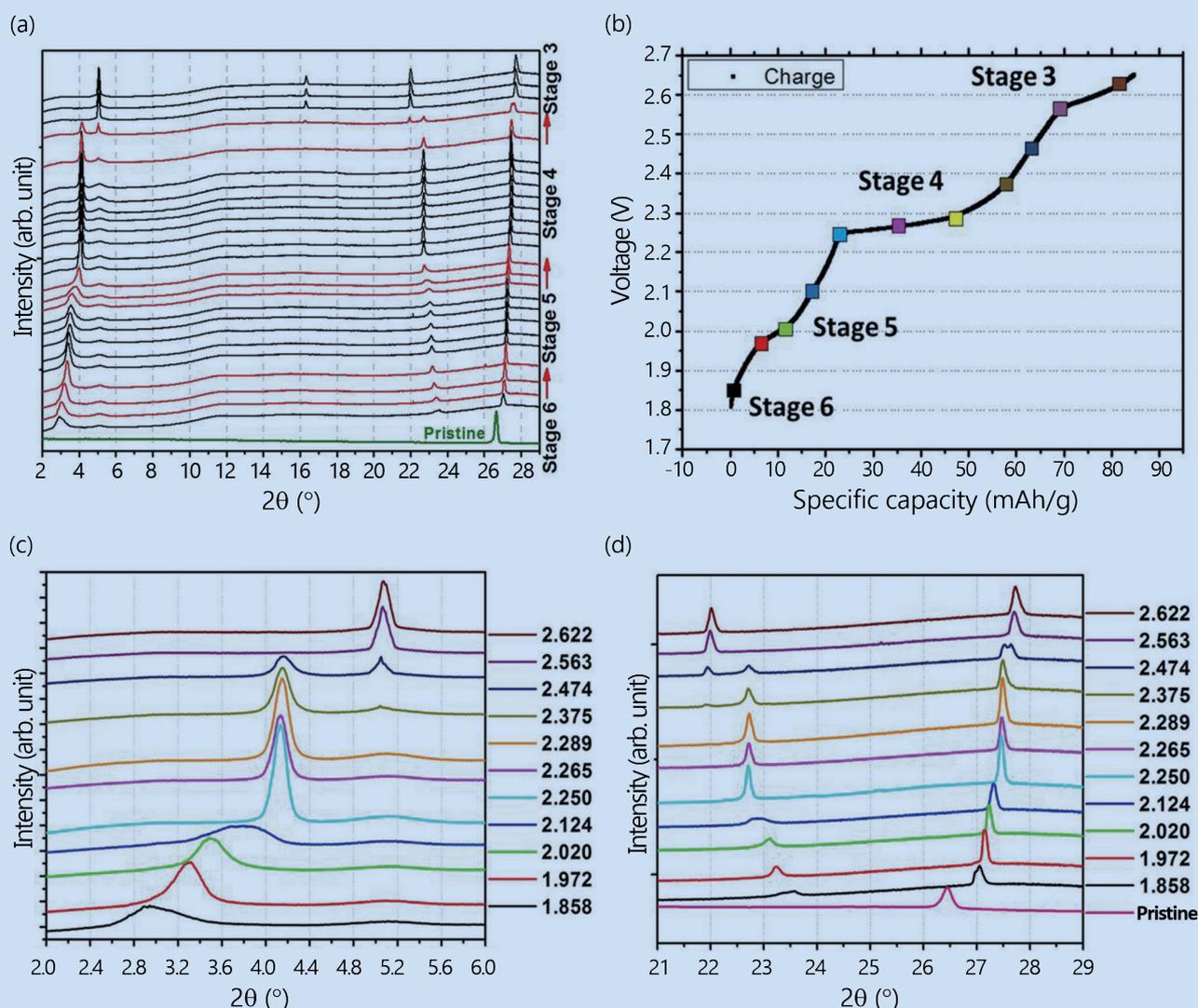


Fig. 1: Synchrotron X-ray diffraction and battery charging *in situ* and *operando*. (a) XRD data of a graphite electrode in an aluminum-graphite battery *in situ* under charging to various voltages at -10 °C under 50 mA/g current. The voltages are in the range 1.858–2.622 V from the bottom to the top curves. The XRD curves are displaced vertically for clarity. Adjacent curves of the same color were recorded along a voltage plateau (indicated at the right with a graphite staging number that is also labeled in the electrochemical charging curve in (b)). (b) Aluminum-graphite battery-charging curve recorded simultaneously with XRD measurement with the corresponding graphite intercalation stages labeled along the curve. XRD data *in situ* in the (c) small-angle and (d) larger-angle regimes showing details of the XRD peak evolutions of graphite during anion intercalation to different stages. The right-hand side labels are charging voltages (in volts). [Reproduced from Ref. 1]

Bing-Joe Hwang (National Taiwan University of Science and Technology) and his co-workers recently investigated rechargeable Al batteries composed of an Al negative electrode, a graphite positive electrode and an ionic-liquid (IL) electrolyte at temperatures down to $-40\text{ }^{\circ}\text{C}$.¹ The reversible battery discharge capacity at low temperatures could be superior to that at room temperature. X-ray diffraction (XRD) experiments *operando* at **TPS 09A** (Fig. 1) were performed to probe the intercalation of chloroaluminate anions into the positive electrode, graphite, during electrochemical charging and discharging *in situ* of rechargeable aluminum batteries. These XRD data indicated that well defined staging and long-range order exist in the anion-graphite intercalation structures.

The XRD data *in situ* indicated electrochemically driven structural evolutions from stage n to stage $n - 1$ ($n = \text{integer}$; a staging number corresponding to every n graphene layers being intercalated with a layer of ions) of the anion-graphite intercalation compound. The results revealed a surprisingly ordered anion-intercalation staging behavior in the graphite despite the large anion size and the remarkably stable graphite structure upon repeated intercalation and deintercalation with the large anions. Specifically, electrochemical and synchrotron XRD experiments *in situ* and *operando* combined with theoretical modeling revealed stable $\text{AlCl}_4^-/\text{graphite}$ intercalation up to stage 3 at low temperatures, whereas intercalation was reversible up to stage 4 at room temperature. The higher-degree intercalation of anion or graphite

at low temperatures affords a rechargeable Al battery with a greater discharge voltage (up to 2.5 V, a record for an Al battery) and energy density.

In summary, the reversible discharge capacity of the battery at low temperatures was superior to that at room temperature because of the increased staging stability and the reversibility of intercalation of chloroaluminate anion in graphite at low temperatures. Electrochemical and synchrotron XRD experiments *in situ* and *operando* combined with theoretical modeling revealed reversible stage 3 intercalation at low temperatures, whereas at room temperature intercalation was stable up to stage 4. A remarkable cycle life and high rate performance were achieved for an Al battery operating at temperatures down to $-30\text{ }^{\circ}\text{C}$ and $-40\text{ }^{\circ}\text{C}$. (Reported by Yan-Gu Lin)

This report features the work of Bing-Joe Hwang and his co-workers published in Proc. Natl. Acad. Sci. USA **115**, 5670 (2018).

TPS 09A Temporally Coherent X-ray Diffraction

- XRD
- Materials Science, Surface, Interface and Thin Films, Condensed-matter Physics

Reference

1. C.-J. Pan, C. Yuan, G. Zhu, Q. Zhang, C.-J. Huang, M.-C. Lin, M. Angell, B.-J. Hwang, P. Kaghazchi, and H. Dai, Proc. Natl. Acad. Sci. USA **115**, 5670 (2018).

Rapid Reconstruction of Amorphous Nanofilms for Bifunctional Electrocatalysts

A facile strategy based on rapid reconstruction of amorphous nanofilm precursors is proposed for the exploration of catalysts free of precious metals.

The development of efficient bifunctional electrodes with extraordinary mass activity and robust stability is an eternal, yet challenging, goal for the water-splitting process. Under conditions of operation of the oxygen-evolution reaction (OER) or the hydrogen-evolution reaction (HER), some perovskite electrocatalysts were recently found to undergo a slow reconstruction over the surface, which transformed into an amorphous phase of thickness $\approx 20\text{ nm}$, resulting in increased activity. For such transformation to be utilized for the development of new electrode materials for water splitting would be highly attractive, but several challenges must be overcome. First, the rate of reconstruction should be significantly increased; for a conventional process reported for perovskite electrocatalysts, a period of several hours is required for the electrode to attain the greatest activity, following which an amorphous film of thickness from several to dozens of nanometers was formed on the surface of the perovskite oxides. Second, charge transfer in the reconstructed electrocatalysts is a great concern, as most perovskite oxides are poor electric conductors near $23\text{ }^{\circ}\text{C}$, which might significantly retard the reaction