

## ALUMINIUM BATTERIES

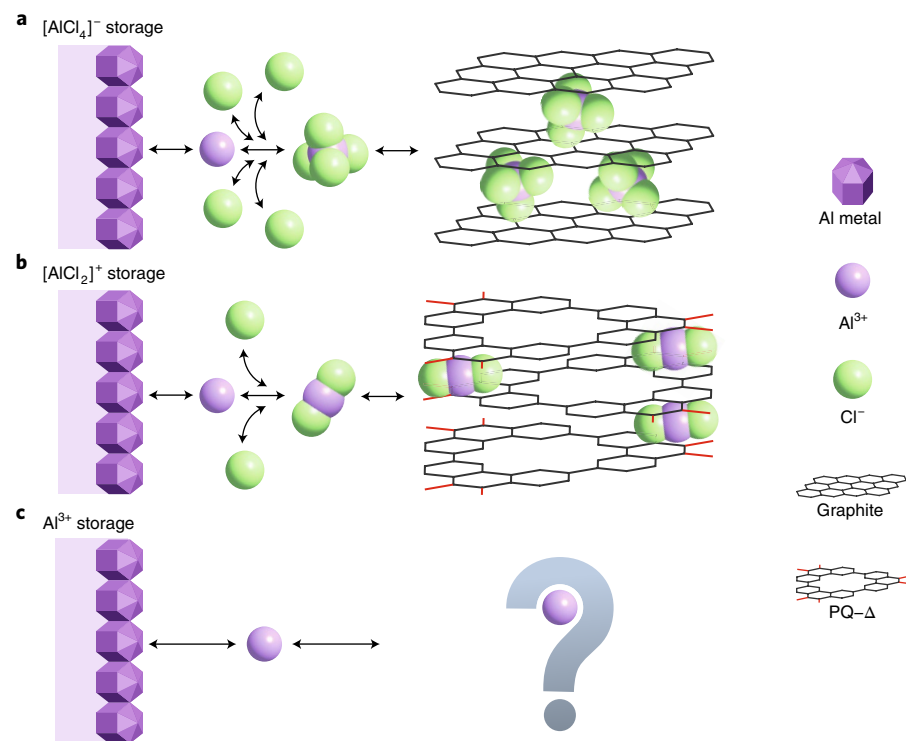
## Halfway through

Aluminium–graphite batteries can reversibly store  $\text{AlCl}_4^-$  ions at their cathodes, but the large consumption of electrolytes reduces their specific energy. Here a cathode based on redox-active triangular organic molecules is shown to be able to take up  $\text{AlCl}_2^+$ , offering hope towards complete Al-ion storage.

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Our climate and energy problems call for a paradigm shift of energy resources from fossil fuels to renewable energies such as solar and wind. However, these renewable energies are intermittent and cannot be relied upon to match patterns of electricity demand. Storage of energy when the sun shines and the wind blows is therefore a key enabler for green energy technologies. Today's energy storage technologies are either geologically limited, such as pumped storage hydropower and compressed air energy storage, or expensive, such as lithium-ion and high-temperature sodium–sulfur batteries. One potential solution to the site dependence and cost issues is rechargeable batteries built with vastly abundant materials and simple designs. Among the emerging low-cost batteries, rechargeable aluminium batteries are particularly appealing because aluminium is the third most abundant element in the Earth's crust and, as an anode material, has one of the highest volumetric capacities and a reasonably low redox potential. The technology has drawn significant research interests since Hongjie Dai's group demonstrated an ultrafast and highly stable aluminium–graphite battery<sup>1</sup>, but a rechargeable aluminium battery with competitive specific energy and cycling stability does not exist yet. Writing in *Nature Energy*, Jang Wook Choi, Fraser Stoddart and colleagues from the USA and South Korea now report an organic cathode material that could eventually lead to efficient storage of aluminium ions and practical rechargeable aluminium batteries<sup>2</sup>.

One of the most attractive characteristics of a rechargeable aluminium battery is its potentially high energy density thanks to the use of an aluminium metal anode. Each mole of aluminium gives out three moles of electron upon discharge, thus putting aluminium's volumetric capacity of  $8,045 \text{ mAh cm}^{-3}$  well ahead of that of other popular metal anodes such as lithium ( $2,046 \text{ mAh cm}^{-3}$ ), sodium ( $1,130 \text{ mAh cm}^{-3}$ ) and magnesium ( $3,837 \text{ mAh cm}^{-3}$ ). However, aluminium ions ( $\text{Al}^{3+}$ ) have strong



**Fig. 1 | Charge storage mechanisms of aluminium batteries.** **a**, An aluminium–graphite battery with the  $\text{AlCl}_4^-$  storage mechanism at the graphite cathode. Each mole of  $\text{Al}^{3+}$  stripped from the aluminium metal anode consumes four moles of  $\text{Cl}^-$  in the electrolyte to form  $\text{AlCl}_4^-$  before entering the cathode. **b**, An aluminium–PQ-Δ battery with an  $\text{AlCl}_2^+$  storage organic cathode. Half the amount of  $\text{Cl}^-$  is involved in the reaction compared with the aluminium–graphite battery. **c**, A true aluminium-ion battery with  $\text{Al}^{3+}$  storage at both electrodes and no consumption of electrolyte during cell operation. No cathode material performs efficiently in this configuration thus far.

coordination interactions with electrolyte species and cathode materials. As a result, conventional intercalation compounds such as metal oxides and sulfides and conversion compounds such as sulfur generally show sluggish kinetics and poor cycling stability<sup>3</sup>. Graphitic cathodes, on the other hand, could bypass the  $\text{Al}^{3+}$  storage and its associated issues by adopting an  $\text{AlCl}_4^-$ -storage mechanism. However, an aluminium–graphite battery is a hybrid-ion battery in which the stored ions are different at the cathode ( $\text{AlCl}_4^-$ ) and the

anode ( $\text{Al}^{3+}$ ) (Fig. 1a), and a large amount of electrolyte is required to sustain  $\text{Cl}^-$  supply and battery operation. The cell energy is thus compromised to below the level of lead-acid batteries<sup>4</sup>, and the advantage of using an aluminium metal anode is negated.

To overcome the above-mentioned dilemma, Choi, Stoddart and colleagues cast their eyes on redox-active organic compounds, an emerging family of versatile and potentially low-cost electrode materials that have enabled many novel battery chemistries<sup>5</sup>. They chose

phenanthrenequinone (PQ) as the redox-active building block and integrated it into a triangular macrocycle (PQ- $\Delta$ ). PQ is known to form PQ-MCl<sub>2</sub>-type complexes with multivalent metal (M) ions<sup>6</sup>, resulting in a unique AlCl<sub>2</sub><sup>+</sup> storage mechanism with (PQ- $\Delta$ <sup>3+</sup>)-3AlCl<sub>2</sub> as the discharge product (Fig. 1b). The macrocyclic molecule crystallizes in a layered structure with strong intermolecular interactions, which renders the compound insoluble. For the first time, this work shows a rechargeable aluminium battery with a cation-storing cathode with competitive performance characteristics including a low voltage hysteresis of 0.08 V, a 64% capacity delivery within 36 seconds, and a 57% capacity retention after 5,000 cycles. A particularly encouraging achievement of the aluminium-PQ- $\Delta$  battery is that the storage of AlCl<sub>2</sub><sup>+</sup> consumes only half the amount of Cl<sup>-</sup> as that consumed by AlCl<sub>4</sub><sup>-</sup> storage. The aluminium-PQ- $\Delta$  battery is therefore half as electrolyte-demanding as an aluminium-graphite battery with the

same capacity, which contributes to a higher specific energy for the former.

Finally, we note that aluminium-PQ- $\Delta$  is still a hybrid-ion battery, which means that the specific energy is still considerably limited by the required amount of electrolyte during operations. The transition from AlCl<sub>4</sub><sup>-</sup> to AlCl<sub>2</sub><sup>+</sup> storage is halfway towards a true aluminium-ion battery in which a unidirectional Al<sup>3+</sup> flow between cathode and anode takes place (Fig. 1c). The successful demonstration by Choi, Stoddart and colleagues of organic electrode materials as hosts for cationic aluminium species could mark the beginning of high-energy aluminium-based batteries. Going forward, the AlCl<sub>2</sub><sup>+</sup> ingress into the cathode host and its solid-state diffusion need more fundamental understanding to guide the design of even better cathode materials. Eventually, Al<sup>3+</sup> storage should be explored on the basis of simultaneous advances of electrolytes with weakly cation-coordinating anions and cathode materials with favourable coordination behaviours.

The cost and availability of current collectors, cathode materials, and other cell components should also be considered during the cell design so that the low cost and abundance of aluminium can be translated into the final devices. □

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