Materials science

Rested batteries can recover lost performance

Laura C. Merrill

In lithium-metal batteries, grains of lithium can become electrically isolated from the anode, lowering battery performance. Experiments reveal that rest periods after battery discharge might help to solve this problem. **See p.306**

Lithium-metal batteries, which use metallic lithium as the anode, show great promise as the next generation of rechargeable batteries. It is generally thought that 'calendar ageing' of these batteries – resting them without an applied current or voltage – results in degradation that permanently reduces the amount of charge that the battery can supply, lowering performance. This loss of battery capacity is typically caused by irreversible reactions occurring between lithium metal and the battery's electrolyte, but it can also be due to lithium metal becoming electrically isolated from the rest of the anode. On page 306, Zhang *et al.*[1] report that electrically isolated lithium metal can reconnect to the anode after calendar ageing of the discharged battery.

To make next-generation batteries smaller and lighter, they should contain active materials that have a greater energy density (energy stored per unit mass) than those used in currently available batteries. Unlike the anodes of lithium-ion batteries, which act as host materials for the active material (the lithium ions), lithium-metal anodes are entirely composed of the active material and therefore have a higher theoretical charge-storage capacity. In lithium-metal batteries, lithium ions are deposited on the anode during charging to form lithium metal, which then dissolves into lithium ions during discharging. The efficiency of this electrodeposition–electrodissolution cycle is used as a metric with which to evaluate lithium-metal battery systems, and is measured in model systems in which lithium is cycled on and off a copper substrate.

"Battery capacity lost through the formation of isolated lithium during cycling can be recovered during calendar ageing."

One might imagine that the lithium anode increases and decreases in size uniformly as lithium is cycled. However, the anode instead often transforms into a mixture of lithium grains and electrolyte-decomposition products. The decomposition products are typically electrical insulators that can surround some of the lithium grains, thus electrically isolating the grains from the rest of the electrode, and resulting in loss of battery capacity.

Calendar ageing is thought to cause irreversible lithium corrosion that is detrimental to battery performance[2–6]. It has been suggested, however, that electrically isolated lithium grains (usually referred to simply as isolated lithium) formed during calendar ageing after charging can reconnect to the anode during subsequent battery cycles[7,8]. An understanding of how calendar ageing affects the performance of lithium-metal batteries is necessary because it might occur in future applications – for example, when battery-powered electronic devices and electric vehicles are not in use.

Zhang *et al.* investigated calendar ageing and the recovery of isolated lithium in discharged systems. In their experiments, lithium was cycled on and off copper substrates in model coin cells (which are similar to the disc-shaped batteries used in watches). Control cells were cycled without resting, and were compared with cells that were cycled and then calendar-aged for 12 hours after discharge.

The authors report that the average Coulombic efficiency of the calendar-aged cells – a measure of the efficiency with which charge is transferred during lithium cycling – was 98.2%. This was higher than the average Coulombic efficiency of the control cells (96.9%). The results suggest that battery

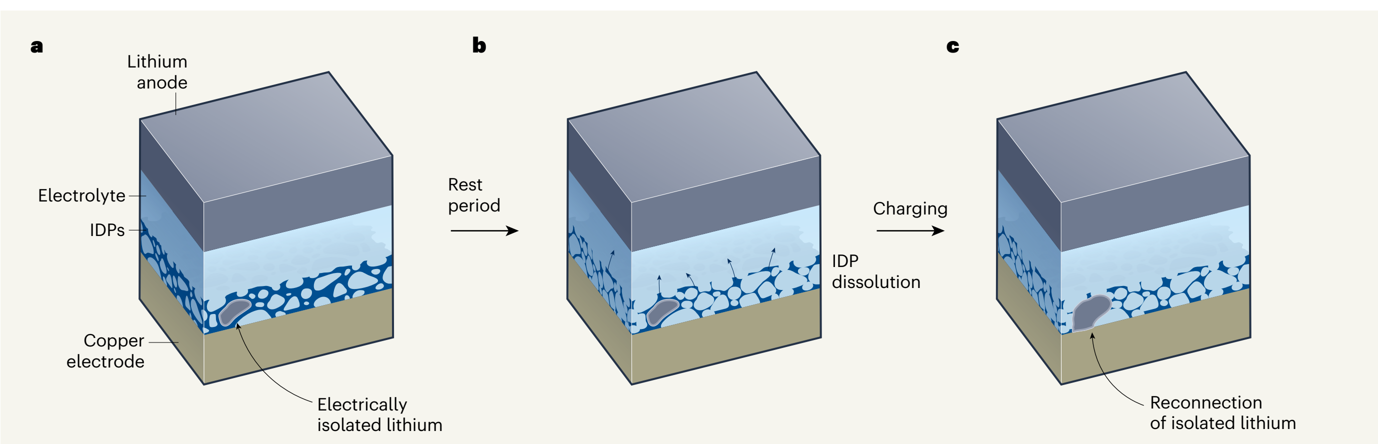

Figure 1 | Proposed mechanism for how discharged lithium-metal batteries recover lost charge-storage capacity. Zhang *et al.*[1] studied cells that model electrochemical processes in lithium-metal batteries. The cells consisted of a liquid electrolyte sandwiched between a lithium anode and a copper electrode. During cell charging, transfer of lithium ions from the anode through the electrolyte results in electrodeposition of lithium metal on the copper; during cell discharging, the reverse process causes lithium metal on the copper to dissolve. The electrolyte partly degrades during charge–discharge cycles, forming electrically insulating decomposition products (IDPs) around grains of the deposited lithium metal. **a**, After discharge, IDPs can surround lithium grains at the copper–electrolyte interface. Such electrically isolated lithium grains cannot take part in charging cycles, lowering cell performance. **b**, Zhang *et al.* observe that, when the cell is allowed to rest, the IDPs dissolve into the electrolyte. **c**, During subsequent charging, the lithium grains can reconnect to lithium deposited on the copper, and thereby take part in charging cycles once again.

capacity lost through the formation of isolated lithium during cycling can be recovered during calendar ageing. This is the opposite of what has typically been reported (irreversible lithium corrosion and loss of capacity) during calendar ageing of charged batteries[2–5].

Zhang and colleagues observed similar capacity recovery during calendar ageing in discharged coin cells when they tested a range of battery electrolytes and cycling conditions, both of which influence the efficiency of lithium-metal cycling. This demonstrated that the phenomenon is general. However, cycling measurements alone cannot prove that the capacity recovery was caused by the recovery of isolated lithium. The authors therefore used several other methods to investigate the capacity recovery, of which operando measurements – in which an optical microscope was used to observe lithium electrodeposition–electrodissolution cycles on a copper mesh electrode in a coin cell over time – provided most insight into the mechanism.

The optical time-lapse data showed that isolated lithium formed as early as the first cycle. However, when aged after discharge, the electrically insulating products of electrolyte decomposition surrounding the isolated lithium dissolved into the electrolyte (Fig. 1). This allowed the isolated lithium to become electrically reconnected to the electrode after subsequent charging.

The small coin cells used by Zhang *et al.* were helpful models for evaluating lithium-metal cycling, but they did not contain a battery cathode. When the authors added a cathode, they observed the same benefits of calendar ageing. It should be noted, however, that addition of a cathode creates a more complex system, the behaviour of which can be difficult to interpret.

The authors also studied capacity recovery in larger pouch cells, a type of battery characterized by soft packaging. These cells contained a cathode made of lithium iron phosphate ($LiFePO_4$, a frequently used lithium-ion cathode material) and a copper substrate. The cells lacked a lithium-metal anode, which both decreases the total mass of the active material in the cells compared with cells that contain lithium-metal anodes and increases the energy density.

During the first charging step of the pouch cells, lithium metal was electrodeposited onto the copper substrate using the cathode as the lithium source. Zhang *et al.* observed that, as in the smaller coin cells, the pouch cells showed signs of capacity recovery after ageing in the discharged state – although further characterization was not carried out to confirm that this was due to recovery of isolated lithium. Nevertheless, the finding suggests that isolated lithium could be recovered to mitigate capacity losses in the large-format, cathode-containing batteries that are likely to be developed for practical applications.

Although the study aids our understanding of calendar ageing and capacity loss in lithium-metal batteries, gaps in our knowledge still exist. For example, the authors implemented a carefully prescribed protocol that enabled recovery of isolated lithium, but it is too soon to say whether this can be translated to consumer applications in which the number of cycles and rest time will vary. The authors also investigated pouch cells that used a low-voltage cathode material, but high-voltage materials will be needed to make batteries that have high energy densities, and this might complicate or accelerate ageing mechanisms. Furthermore, this work did not study ageing in partly charged or partly discharged cells; this should be evaluated, given that ageing might occur in such states in practical applications. Nevertheless, Zhang *et al.* offer a crucial perspective: calendar ageing might not be detrimental to the performance of lithium-metal batteries, and could be used to improve it.

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The author declares no competing interests.

Forum: Microbiology

The journey to understand previously unknown genes

The analysis of DNA sequences sheds light on microbial biology, but it is difficult to assess the function of genes that have little or no similarity to characterized genes. Here, scientists discuss this challenge from genomic and microbial perspectives. **See p.377**

The topic in brief

- **Some aspects of microbiology remain mysterious because of a lack of information about the identity and role of many microbial genes and proteins.**
- **The ability to obtain and analyse microbial sequences at scale and across species, including those that cannot be grown under laboratory conditions, are providing insights and data to explore.**
- **Writing in *Nature*, Rodríguez del Río *et al.*[1] report their analysis of 149,842 bacterial genomes sampled from a variety of habitats in the wild.**
- **The data were used to select sequences to generate a catalogue of 404,085 previously unknown gene families that could be prioritized for further study.**
- **The investigation of these previously unknown genes could lead to new clinical tools or offer fresh perspectives about how microorganisms evolved to survive in their natural environments.**

Jakob Wirbel & Ami S. Bhatt

Bringing structure and context to gene mysteries

The function of most microbial genes is unknown. Some of this microbial 'dark matter' might encode previously unknown types of enzyme or classes of antibiotic. As ever more genes of unknown function are discovered through sequencing of DNA from mixtures of multiple genomes, termed metagenomic sequencing, the difficulty of experimentally characterizing these enigmatic genes has led to a focus on computationally predicting their function[2]. Two publications in *Nature*, one on page 377 by Rodríguez del Río *et al.*[1], and one by Pavlopoulos *et al.*[3] published last October, tackle this challenge by cleverly leveraging advances in clustering algorithms (computational tools that group genes on the basis of similarities in amino-acid sequence) and protein-structure prediction tools[4] such as AlphaFold.

Despite distinct technical approaches,