

insights into the evolution of the folds-to-fat vocalization method. A U-fold opposite a fat cushion has been found in the larynges of all whales examined until now⁶, prompting Elemans and colleagues to suggest that this sound-production method was probably present in the ancestors of modern whales. Thickened U-folds were found only in humpback and bowhead whales (*Balaena mysticetus*), indicating that this characteristic was acquired later during whale evolution. Thicker U-folds are more mobile than the thinner ones of other whales and they can meet to seal the gap between them, allowing them to function as vocal folds. This indicates that whales have either independently acquired or regained the fold-to-fold vocalization method used by land mammals, in addition to the folds-to-fat vocalization method.

In land mammals, vibrations of the vocal folds produce sound (pressure waves) in the air. However, given that whales vocalize underwater, how does the sound get transferred to the water? Future work should address this step of sound generation.

The main limitation of Elemans and colleagues' work is that the authors could test only isolated larynges, removed from the whales' bodies, that were then artificially suspended in air. The natural path of sound production by the vibrating whale larynx therefore remains unknown. Modelling the surrounding tissues in a more 'fleshed-out' experimental design might uncover the full sound-production pathway of whales.

The evolutionary picture will not be complete until we understand how an air-driven system, which generates sound in air and transfers it to the mouth of land mammals, became adapted to work under water for whales. This, in turn, might help us to decipher how baleen whales generate unusual sounds, such as the 'Star Wars' or 'boing' sounds of minke whales and the 'gunshot' sounds of right whales^{18–20}.

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The author declares no competing interests.
This article was published online on 21 February 2024.

Electrochemistry

Solvent trick boosts battery performance

Chong Yan & Jia-Qi Huang

Small solvent molecules have been found to enable a previously unknown ion-transport mechanism in battery electrolytes, speeding up charging and increasing performance at low temperatures. **See p.101**

Two issues that limit the further development of lithium batteries are the lengthy charging times and the poor performance of these batteries at low temperatures¹. One of the most effective solutions to these problems is to upgrade the electrolyte^{2,3} – the material that acts as the 'blood' of the battery by enabling the flow of lithium ions between the electrodes. On page 101, Lu *et al.*⁴ report that organic solvents consisting of small molecules can greatly improve ion mobility in lithium-ion-battery electrolytes, enabling fast charging and impressive battery performance at temperatures as low as –80 °C.

Most electrolytes of lithium-ion batteries consist of one or more lithium salts dissolved in an organic solvent. An ultraconcentrated aqueous solution of a lithium salt – referred to as a water-in-salt electrolyte – is now emerging as a useful alternative⁵. When an electrolyte is injected into the porous electrodes of a lithium-ion battery, it rapidly fills the pores. The result is a medium that allows lithium ions to pass from one electrode to the other but does not conduct electrons.

When lithium salts dissolve in a solvent, their crystalline structure fully disintegrates. This process is driven partly by entropy, a measure of disorder: the second law of thermodynamics favours increases in entropy, and the ions in a salt become much more disordered when they are liberated from an ordered crystal lattice. A bigger driver of dissolution comes from enthalpy, a measure of the total energy of a system. Strong electrical interactions between lithium ions and the solvent molecules result in the formation of solvation structures, in which a central lithium ion is surrounded by bound solvent molecules. This is

a thermodynamically favourable process, because it lowers the enthalpy of the system.

The solvent molecules in solvation structures can adopt various arrangements that depend, for example, on the concentration of the electrolyte solution^{6–8}. When there is strong binding between a lithium ion and its primary solvation sheath (the first layer of molecules and ions around the lithium ion), the whole solvation structure moves with the lithium ion during its translational motion. This is known as vehicular transport (Fig. 1a).

It might be assumed that the speed of lithium-ion transport in battery electrolytes is strongly associated with the arrangement of molecules and ions in solvation structures, which, in turn, is governed by the solvent properties and the concentration of the lithium salt. Such a model would suggest that lithium ions with smaller solvation structures move faster through the electrolyte. This is indeed true in the case of vehicular transport, especially for small solvent molecules and when the number of molecules in the primary solvation sheath is low⁹.

Sometimes, however, this mechanism alone cannot account for exceptionally high ion mobilities, such as those observed for the transport of protons (hydrogen ions, H⁺) in aqueous electrolytes. Protons associate with water molecules in aqueous solutions to form hydronium ions (H₃O⁺), and this allows protons to be passed between neighbouring water molecules like batons in a relay race. This relay mechanism is termed structural transport (Fig. 1b), because it depends on a particular solvation structure that enables ions to 'hop' between molecules. Structural transport boosts the ionic conductivity of aqueous

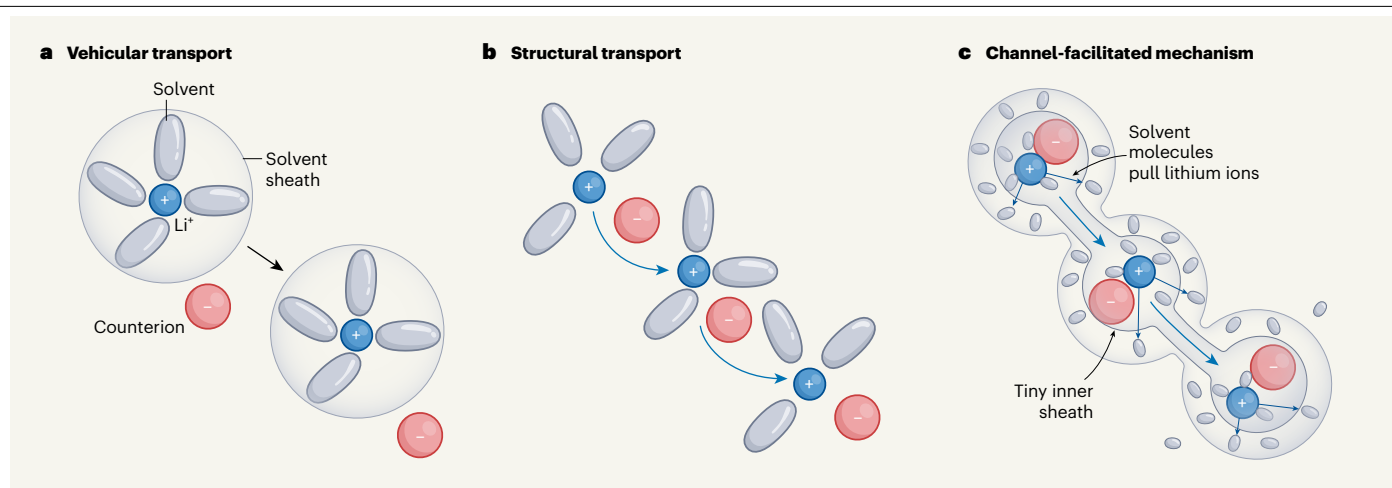


Figure 1 | Mechanisms of ion transport in battery electrolytes. Lithium ions were thought to travel through battery electrolytes in two main ways. **a**, In vehicular transport, the ion carries a sheath of solvent molecules as it moves. Larger solvent molecules hinder transport. **b**, In structural transport, the ions form complexes with one or more solvent molecules, and so can hop between

molecules. **c**, Lu *et al.*⁴ found that very small solvent molecules can form two sheaths around lithium ions. The tiny inner sheaths contain solvent molecules and counterions to the lithium ions. The outer sheaths contain only solvent molecules; these pull lithium ions out of the inner sheath and so generate channels through which the lithium ions can pass, boosting ion mobility.

protons to magnitudes about 100 times higher than those of lithium-salt solutions in organic solvents at $-60\text{ }^{\circ}\text{C}$ (refs 4, 10), and explains why batteries with aqueous electrolytes can operate at temperatures as low as $-100\text{ }^{\circ}\text{C}$ (ref. 10).

It is generally accepted that lithium ions in liquid electrolytes can be transported through either a vehicular or a structural mechanism, or by a combination of both, depending on the concentration of the lithium salt. High concentrations activate the structural transport mechanism, for example¹¹. However, the degree to which the size of the solvation structure determines the transport mechanism has been generally overlooked. Lu *et al.* now propose that, when the solvent molecules are very small, the correspondingly tiny solvation structure can enable a new type of structural transport.

The authors began their study by using analytical experiments and computational modelling to identify an electrolyte that had a particularly promising combination of physical properties for promoting lithium-ion conductivity. Sure enough, when the Lu and colleagues tested this electrolyte (a solution of a lithium salt in a solvent called fluoroacetonitrile, or FAN), it had an ultrahigh ionic conductivity of 40.3 millisiemens per centimetre at $25\text{ }^{\circ}\text{C}$. Moreover, it retained an ionic conductivity of 11.9 mS cm^{-1} at $-70\text{ }^{\circ}\text{C}$, which is more than 10,000 times higher than that achieved by a conventional electrolyte at the same temperature.

Using molecular dynamics simulations, Lu *et al.* showed that the small size of the FAN molecules promotes solvation in which two sheaths form around the lithium ions. The primary solvation sheath contains not only solvent molecules, but also the counterions to the lithium ions. A second layer of solvent molecules also forms; this pulls lithium ions out

of the primary solvation sheath and thereby generates channels through which the lithium ions can pass, enhancing transport (Fig. 1c). This previously unknown form of structural transport could inspire innovative approaches to fast charging and to the development of low-temperature batteries.

Batteries are complex systems that integrate materials science, electrochemical science and intercalation science (the study of the reversible insertion of ions into other materials). Coordinating the many factors that contribute to battery performance is like conducting a symphony, in which each musical instrument has a crucial role. Thus, the authors' transport mechanism will almost certainly need to be used with other design features to develop batteries that charge rapidly and work at low temperatures.

“This study opens up avenues of research for developing the next generation of lithium-ion batteries.”

The potential lack of compatibility between the small solvation structures and the materials used to make positive and negative electrodes is also a problem that will need to be carefully considered in battery design. Constituents of the solvation structures could undergo redox reactions during battery charging and discharging, forming surface layers on the electrodes that greatly affect the cycling life and fast-charging ability of batteries^{12,13}. Lu *et al.* found that their new electrolyte promotes the formation of a conductive layer on the electrodes in their experiments, which aids charging and supports the use of batteries at

very low temperatures, suggesting that it has good compatibility with both positive and negative electrodes⁴.

Lu and colleagues' research opens up avenues of research for developing the next generation of lithium-ion batteries. More broadly, the reported ion-transport mechanism could also be useful for energy-storage systems that use ions of metals other than lithium as charge carriers, such as sodium, potassium, magnesium and calcium ions.

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The authors declare no competing interests. This article was published online on 28 February 2024.