

BATTERIES

Opening the window for aqueous electrolytes

Lithium batteries can operate with a safer “water-in-salt” electrolyte

By Leland Smith and Bruce Dunn

Facilitating ion motion between electrodes, electrolytes help to harness the chemical energy in a battery to produce a current and supply usable electric power. Among liquid electrolytes, there are traditional solutions of salt dissolved in solvents (aqueous or organic) and ionic liquids. Lithium-ion batteries, whether for consumer electronics or electric vehicles, have used nonaqueous liquid electrolytes because of their higher voltage stability. Although aqueous electrolytes would be safer and more environmentally benign, the electrochemical voltage window (1.23 V) precludes the use of high-voltage electrode couples that enable the high energy density of lithium-ion batteries. On page 938 of this issue, Suo *et al.* (1) change this perception by demonstrating an operating window of 3 V created by increasing the salt concentration to form “water-in-salt” electrolytes.

The voltage and charge stored in an electrochemical cell are determined by the chemistry of the electrodes. However, for a given pair of electrodes, it is only possible to build a viable electrochemical cell if there is an electrolyte that can remain stable against the electrode components over the voltage range. For aqueous systems, the thermodynamic voltage limit is 1.23 V, although there are kinetic considerations that may cause the measured voltage for water breakdown to deviate from the theoretical value (2). Indeed, important work in electrocatalysis is devoted to decreasing those kinetic limitations (3). Nonetheless, as the cell voltage increases beyond 1.23 V, water electrolysis will begin to dominate the cell chemistry.

The electrolysis of water produces gaseous products (H_2 and O_2) that depart the electrode-electrolyte interface, freeing up the electrode surface so that more electroly-

sis can occur. For other electrolyte-electrode combinations, electrolyte breakdown can result in the formation of insoluble solid materials at the electrode surface (4). These decomposition products can widen the effective voltage stability range of the electrolyte above the thermodynamic value.

The electrolyte solvent, salt, and electrode may all contribute to the formation of solid materials at the electrode-electrolyte interface. Such interfacial layers play a central role in many of today's commercially important batteries. For example, a

ceeding what is typically obtained from aqueous electrolytes. The high stability is attributed to the electrochemical reduction of bis(trifluoromethane sulfonyl)imide at the anode surface, which forms an SEI layer consisting primarily of LiF, and is accompanied by a shift in the oxygen evolution reaction to higher voltages (1).

The most obvious benefit of the water-in-salt electrolyte is an increased variety of available lithium electrode materials as compared to traditional water-based electrolytes, as seen in the figure. Although organic

electrolytes provide a wider voltage window, Suo *et al.* suggest that with a window of 3 V, energy densities of 100 Wh/kg are attainable. The development of batteries offering such high energy density plus the safety advantages of an aqueous electrolyte is certain to have an impact, especially in the area of consumer electronics. Moreover, the use of a water-tolerant electrolyte is likely to improve recycling and reclamation efforts as well as offer the opportunity to fabricate lithium-ion batteries without the need for expensive dry rooms. There is also the likelihood that such water-in-salt electrolytes can be applied to salts that are less expensive than

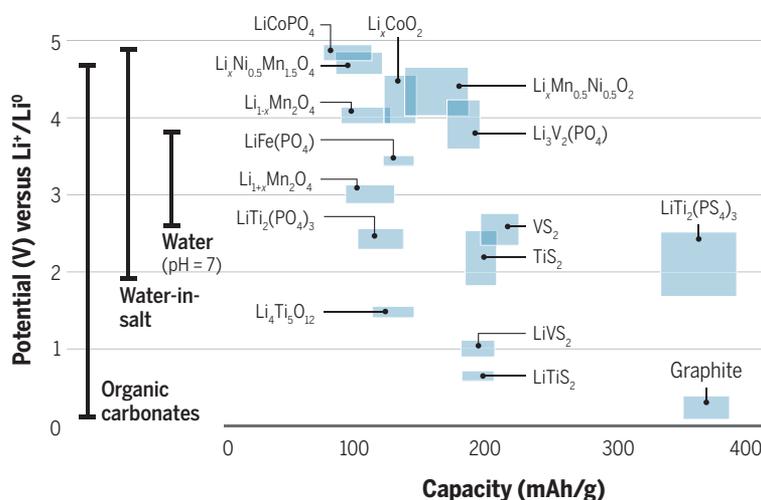
lithium bis(trifluoromethane sulfonyl)imide, as well as to other battery chemistries. The latter may be especially important for the rapidly emerging field of sodium-ion batteries, which potentially offer a lower cost per watt-hour than lithium-ion batteries (6). ■

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A new type of solid-electrolyte interphase (SEI) layer. The voltage stability limits of organic, water-in-salt, and aqueous (pH = 7) electrolytes are compared to the chemical potential of various lithium intercalation materials. The discovery of SEI formation in water-based electrolytes is an exciting development for aqueous lithium and beyond-lithium battery chemistries.

$PbSO_4$ film at the electrode surface allows lead-acid batteries to operate at ~2.0 V, well beyond the thermodynamic limit of water electrolysis (5). In lithium-ion batteries, the decomposition of organic liquid electrolytes at the anode results in the formation of an interfacial layer containing species such as Li_2CO_3 and LiF, in addition to organic materials (3). This solid-electrolyte interphase (SEI) allows organic electrolytes in lithium-ion batteries to operate at potentials below their thermodynamic stability limit of ~0.8 V versus Li/Li^+ (3).

The work of Suo *et al.* presents an exciting new development in the area of solid interfacial layers. Highly concentrated (>20 mol/kg) aqueous mixtures of lithium bis(trifluoromethane sulfonyl)imide yielded a voltage stability window of 3.0 V, far ex-

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