

## Na Metal Anode: “Holy Grail” for Room-Temperature Na-Ion Batteries?

Wei Luo and Liangbing Hu

Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, United States

Issues such as fossil fuel depletion, environmental pollution, and global warming have triggered much interest in clean/renewable energy sources and the development of electric vehicles (EVs). To address these issues, advanced energy conversion and storage technologies play a crucial role. With relentless efforts in the past decades, Li-ion batteries (LIBs) have become the primary source to power portable electronic devices. Scientists and engineers now direct their attention to the use of LIBs in EVs and grid scale energy storage due to their high energy density and long lifetime.<sup>1</sup> Despite LIB's promising performance, lithium sources are relatively limited and unevenly distributed across the globe. Inevitably, LIBs will become unaffordable and large-scale production will falter. Just one row down from lithium on the periodic table and the sixth most abundant element in Earth's crust, sodium (Na) is a promising alternative to lithium for energy storage technologies. Additionally, seawater is a nearly infinite potential resource for Na, which makes Na-based batteries attractive for grid scale energy storage.<sup>2</sup>

In the 1970s, sodium–sulfur (Na–S) batteries with naturally abundant materials (Na metal anodes and S cathodes) achieved reasonable energy densities using  $\beta$ -alumina electrolytes.<sup>3</sup> However, high operating temperature (270–350 °C), expensive electrolytes, and additional safety concerns hampered further development of Na–S batteries. Recently, attention has shifted to room-temperature Na-ion batteries (NIBs), which are analogous to conventional LIBs within a liquid electrolyte system. Over the past few years, significant progress has been made on NIB cathode materials.<sup>2</sup> The challenge of NIBs remains the anode since the commercial anode for LIBs, graphite, is not compatible with NIBs with a poorly understood failure mechanism. To date, only a few anode materials such as hard (nongraphitizable) carbon and metal alloys exhibit reasonable performance.<sup>4</sup> On the other hand, Na metal anodes show great potential due to their high theoretical capacity (up to 1166 mAh/g) and low redox potential, which are important for room-temperature Na–S or

### Yi Cui and co-workers developed a stable sodium metal anode solution. How could this fulfill a longstanding promise?

Na–O<sub>2</sub> batteries.<sup>5,6</sup> Nonetheless, studies on Na metal anodes are scarce. Researchers may presume that Na metal anodes will fail in room-temperature NIBs since Li metal anodes have previously failed in LIBs due to safety concerns and poor cycling performance. Although Li metal anodes are regarded as the “Holy Grail” in LIBs,<sup>7,8</sup> significant challenges still remain.

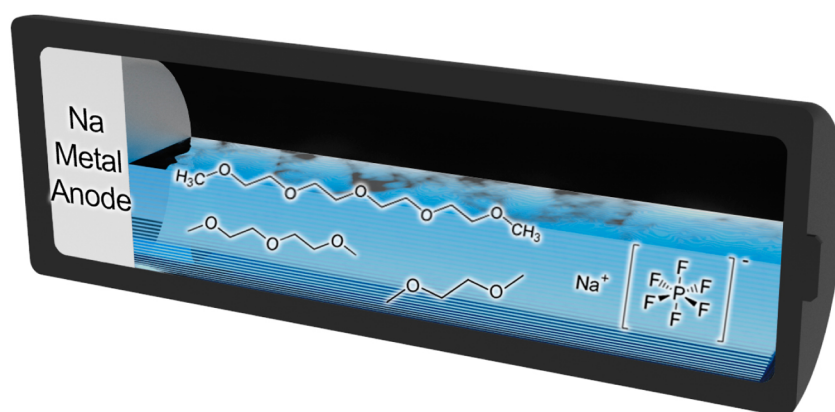
This new finding suggests that a uniform and compact inorganic SEI is highly impermeable to the electrolyte solvent, which prevents further contact between the electrolyte and the Na metal.

Is the low redox potential and high capacity Na metal anode the “Holy Grail” for room-temperature NIBs?

Now, writing in this issue of *ACS Central Science* Yi Cui and colleagues<sup>9</sup> report a simple solution to achieve a highly reversible Na metal anode for room-temperature NIBs (Figure 1). The new pathway employs a simple liquid electrolyte: NaPF<sub>6</sub> (sodium hexafluorophosphate) in glymes (mono-, di-, and tetraglyme). This new discovery not only takes a great step toward achieving high performance room-temperature NIBs but also promotes additional research efforts related to Na metal anodes.

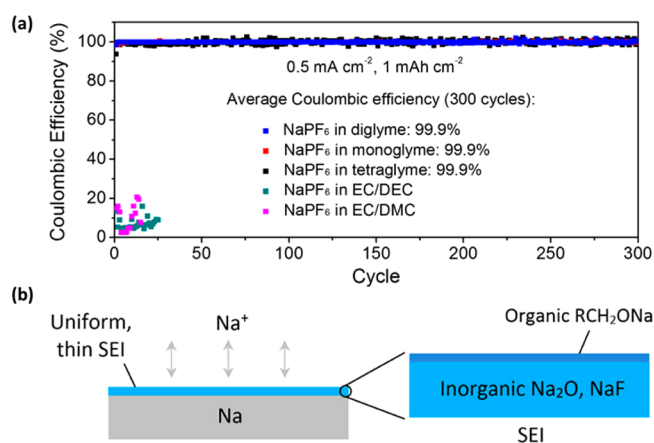
Today, the commercial LIBs in your smart phone or laptop employ carbonate-based organic electrolytes. Li metal anode cannot function well in this type of electrolyte system.<sup>10</sup> The major challenges include: (1) formation of mossy Li leading eventually to Li dendrite; (2) high activity

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**Figure 1.** NaPF<sub>6</sub>–glyme electrolytes enable the use of promising Na metal anodes for room-temperature Na-ion batteries. Image courtesy of Jiaqi Dai from the University of Maryland.

with electrolyte; (3) safety concerns extending from the exothermic reaction nature. In the present study, Cui and co-workers found that nonuniform and/or dendritic deposition also occurs for Na metal anode in NaPF<sub>6</sub>–carbonate electrolyte system with a low Coulombic efficiency (CE). Surprisingly, when the carbonate solvent is replaced by glymes, stable cycling performance (99.9% CE over 300 cycles) is achieved (Figure 2a). They identified



**Figure 2.** (a) Coulombic efficiencies of Na metal anodes cycled using NaPF<sub>6</sub> in various electrolyte solvents. (b) Schematic showing the SEI formed on the Na metal surface using the NaPF<sub>6</sub>–glyme electrolyte.<sup>9</sup> Reprinted with permission from ref 9. Copyright 2015 American Chemical Society.

that the deposition of Na in the NaPF<sub>6</sub>–glyme electrolyte system is quite uniform and no dendritic Na is formed upon cycling.

By comparing these electrolyte components, Cui et al. found that both salt and solvent play a critical role in forming a uniform and compact inorganic SEI near the electrode surface.

To reveal the mechanism responsible for the excellent performance, Cui and his team investigated the solid-electrolyte-interphase (SEI) that formed on the electrode in various electrolytes via ex situ X-ray photoelectron spectroscopy (XPS). It was found that the SEI in this NaPF<sub>6</sub>–glyme system consisted of both organic species (sodium alkoxides, RCH<sub>2</sub>ONa) and inorganic species (Na<sub>2</sub>O and NaF). However, the interior SEI was mainly inorganic Na<sub>2</sub>O and NaF species (Figure 2b). This new finding suggests that a uniform and compact inorganic SEI is highly impermeable to the electrolyte solvent, which prevents further contact between the electrolyte and the Na metal. Additionally, the high shear moduli of Na<sub>2</sub>O (49.7 MPa) and NaF (31.4 MPa) can considerably suppress the growth of dendritic Na. To further support the proposed mechanism, SEI compositions were studied using various electrolytes [e.g., NaPF<sub>6</sub>–carbonate, NaN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>–diglyme, NaN(SO<sub>2</sub>F)<sub>2</sub>–diglyme, NaSO<sub>3</sub>CF<sub>3</sub>–diglyme, and NaClO<sub>4</sub>–diglyme] and the results verified that both organic and inorganic species were contained within the SEI interior. The organic SEI products were porous and more permeable to the electrolyte solvent. By comparing these electrolyte components, Cui et al. found that both salt and solvent play a critical role in forming a uniform and compact inorganic SEI near the electrode surface. For example, NaPF<sub>6</sub> has a higher reduction potential than glymes, which results in the preferential reduction of NaPF<sub>6</sub> and the formation of inorganic SEI species. Furthermore, carbonate solvents are more likely to decompose compared to those made from glymes. This trend is attributed to the higher reduction potentials of carbonate solvents, which lead to an increase in undesirable organic species in the SEI near the Na metal anode.

To achieve widespread implementation of Na metal anodes, both a high rate capability and capacity are essential. The uniform and compact inorganic SEI formed in the optimized electrolyte (NaPF<sub>6</sub>–glymes) enables the Na metal

anode to exhibit high average CE values of 99.6% and 99.2% at high current rates of 2 and 4 mA/cm<sup>2</sup>, respectively. When a high capacity of 10 mAh/cm<sup>2</sup> is set, the average CE reaches 100.0% without any dendritic Na formation. To further demonstrate this system's performance, a room-temperature Na–S battery was assembled with a high capacity of 776 mAh/g and good cycle stability.

In closing, the findings of this study could be a significant breakthrough for large scale energy storage technologies by employing a low cost Na-based chemistry solution. The next challenge will be to figure out how to couple this Na metal anode with compatible cathode materials. High energy-density room-temperature Na–S and Na–O<sub>2</sub> batteries will significantly benefit from the development of the Na metal anode system described in this work, and the transfer of knowledge from Li–S and Li–O<sub>2</sub> batteries could also promote future Na-based energy storage technologies.

#### Author Information

E-mail: [binghu@umd.edu](mailto:binghu@umd.edu).

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