Solid state batteries: Sodium is the new lithium

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In the intensive search for novel battery architectures, the spotlight is firmly on solid-state lithium batteries. Now, a strategy based on solid-state sodium-sulfur batteries emerges, making it potentially possible to eliminate scarce materials such as lithium and transition metals.

Solid-state batteries (SSBs) – where the liquid electrolyte is replaced with a solid ionic conductor – are at the forefront of developing post-lithium-ion batteries[1]. Currently, lithium-based ionic conductors and transition metal-based cathodes are the primary focus in the development of SSBs. However, sustainable energy storage solutions require materials that are more abundant and less socially critical than lithium and transition metals.

Replacing lithium with sodium in SSBs at first glance seems promising because of the abundant availability of the latter. Furthermore, the less polarizing sodium ions are in principle more mobile in a solid ionic conductor than lithium, which could lead to faster charging times; it could also offer the possibility of using thicker electrodes, which would, in turn, deliver higher capacities and energy density. However, the development of sodium-based solid-state batteries has been hindered mainly due to the chemical instability of sodium-ion conducting solid electrolytes.

Writing in *Nature Communications*, [2] Yan Yao, Steve W. Martin and coworkers in the USA demonstrate high chemical stability of a novel sodium-ion solid ionic conductor, the oxysulfide glass, $Na_3PS_{4-x}O_x$. The researchers report that the glass electrolyte also enables the use of sulfur – an industrial waste product thus alleviating the use of transition metals – as a conversion cathode, and a metallic sodium anode.

Unlike lithium-sulfur and solid-state lithium-sulfur batteries, sodium-sulfur and its solid-state counterparts are much less developed. In particular, it has been challenging to operate room-temperature sodium-sulfur batteries. Commercialized sodium-sulfur batteries need to run at

elevated temperatures of around 300°C to be above the melting point of sulfur.[3] With their glassy electrolyte, Yao and team are able to achieve stable cycling of solid-state sodium-sulfur batteries at a much-reduced temperature of 60°C.

Key to the success of Yao and team is their careful compositional control of $Na_3PS_{4-x}O_x$ at room temperature. As $Na_3PS_{4-x}O_x$ comprises various thiophosphate- and phosphate-type units, a structural adjustment of these units significantly affects its properties such as the ionic conductivity as well as the stability of the interface with sodium metal. Yao and team report that by introducing a small amount of oxygen, the electrolyte can be processed – via a cold-pressing – into a dense and homogeneous material with either good ionic conductivity or good stability against sodium metal depending on the oxygen content. For example, when x = 0.15, the electrolyte shows higher ionic conductivity; when x = 0.60, the electrolyte is more mechanically and chemically stable.

The researchers then design a tri- or bi-layer electrolyte separator (Fig. 1), with either the $Na_3PS_{3.4}O_{0.6}|Na_3PS_{3.85}O_{0.15}|Na_3PS_{3.4}O_{0.6}$ or $Na_3PS_{3.85}O_{0.15}|Na_3PS_{3.4}O_{0.6}$ configuration, respectively. That is, the more stable composition is exposed to the metal anode whereas the faster conducting composition is further away in the separator. Remarkably, the separator design overcomes the discharge limit (i.e. the reaction of Na and S to Na_2S_4, which is associated with a theoretical capacity of 558 mAh/g) of conventional high-temperature sodium-sulfur batteries. It enables a complete conversion reaction of S to Na_2S, with a theoretical capacity of 1675 mAh/g.

Overall, the work by Yao and team provides an important extension of previous work on oxysulfides in solid electrolyte systems,[4] connecting the local glass forming building units to the chemical, mechanical, and ionic transport properties. It elegantly shows how minor compositional differences in electrolytes can affect battery performance. Moreover, it further substantiates that there is no “one composition fits it all” approach in SSBs; instead, a solid electrolyte consisting of compositions with optimized properties could be useful.

The strongest impact of this work will likely be in opening an avenue for development of solid-state sodium-sulfur batteries. It is increasingly clear that conversion-type cathode chemistry for SSBs can achieve high capacities and at the same time reduce materials costs.[5] Whereas solid-state lithium-sulfur systems are increasingly well performing at room temperature, the operation temperature for solid-state sodium-sulfur batteries needs to be substantially reduced. This could be achieved by using faster ionic conductors as catholytes. In comparison to other Na-ion solid ionic conductors, the ionic conductivity of the oxysulfides of Yao and team is still too low – especially for an areal loading of sulfur higher than 0.15 mg cm^{-2} – to achieve realistic applications. The low ionic conductivity in turn still requires temperatures

above room temperature for operation, which simultaneously helps the uniform metal plating, that is observed in the work of Yao and team.

Following on from their work, it will be important to investigate how more realistic loadings, lower temperatures closer to room temperature and higher current densities together with long-term battery operation can be achieved. Nevertheless, this work elegantly shows how minor compositional differences can affect the overall local chemical composition, the decomposition kinetics at the interfaces, and the resulting properties of the formed decomposition interphases. Given the encouraging results of this work and the vast improvements of performance and understanding made over the last decade in SSBs,[6] sodium may become the new lithium in sulfur-based SSBs.

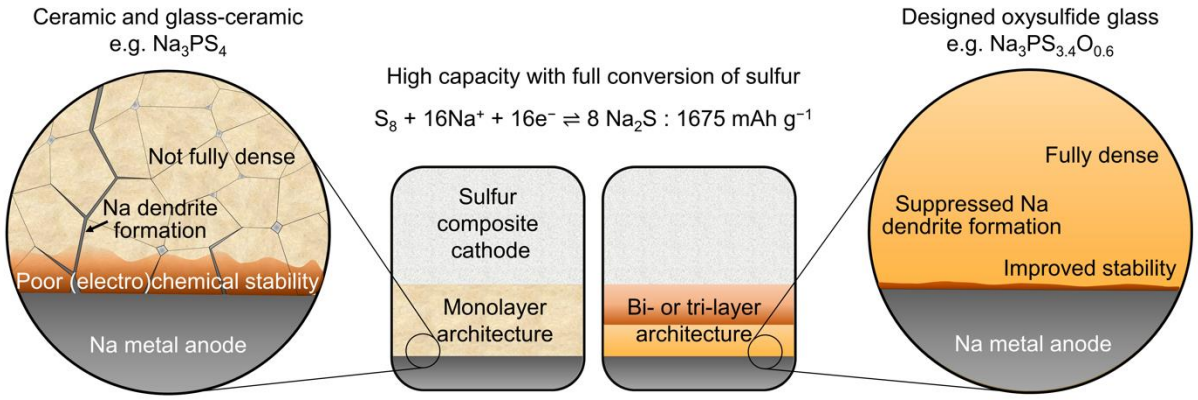

Fig. 1| ***Oxysulfide glass enabling the use of Na metal anode in solid-state sodium sulfur batteries.*** *Na dendrites are known to preferentially form along the grain boundaries with conventional ceramic and glass-ceramic electrolytes (left side). The $Na_3PS_{4-x}O_x$ oxysulfides developed in the work of Yao and the team, which become fully dense upon room-temperature pressure sintering, can successfully suppress the dendrite formation and improve the critical current density. With the multilayer separator architecture, their approach allows the use of sulfur as the cathode active material (right side), opening up the new avenue for room-temperature sodium-sulfur batteries.*

The authors declare that they have no competing interest.

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