

IT TAKES TWO:

Investigating the Ideal Combination of Electrolytes for Bilayer All-Solid-State Batteries

High-capacity, long-life batteries, such as all-solid-state batteries (ASSBs), are a key component of achieving a sustainable, energy efficient society in the future. Of these, bilayer ASSBs—which use a combination of solid electrolytes—are seen as an exciting option that can overcome the limitations of present ASSBs such as comparatively lower conductivity. But bilayer ASSBs come with their own disadvantage of chemical instability between the different solid electrolytes. While there has been some research conducted on this incompatibility, much of it is inconsistent and lacking in detail.

Recognising this gap, a team of researchers from the Research Institute for Sustainable Energy (RISE), one of the five centres of excellence under The Chatterjee Group Centres for Research and Education in Science and Technology (TCG CREST), decided to thoroughly investigate the chemical reactivity between halide solid electrolytes (HSEs) and sulphide solid electrolytes (SSEs). The study, conducted by Lily Mandal, Dr. Abhik Banerjee, Dr. Subha Samanta, Susmita Bera, Dr. Ripan K. Biswas, and Sukanta Mondal provides valuable guidelines for selecting the optimal HSE/SSE bilayer for all-solid-state batteries (ASSBs). Their findings have been published in [ACS Energy Letters](#).

In a bilayer ASSB, a cathode-facing HSE is combined with an anode-facing SSE, tackling two critical issues: the instability of HSEs against Li metal and the instability of SSEs against high-voltage cathodes. However, this configuration also creates an additional interface between the two solid electrolytes. *“For a battery to have a long life, this interface needs to be stable. However, there is a risk of the interface deteriorating and becoming unstable over numerous charge–discharge cycles,”* notes Dr. Mandal. *“Our research was motivated by a desire to find the best HSE/SSE combo.”*

For their study, the research team used HSEs with the chemical formula Li_3MCl_6 , where M represents a central metal atom such as indium, yttrium, scandium, erbium, etc. They fabricated bilayer batteries using these HSEs along with $\text{Li}_6\text{PS}_5\text{Cl}$, an SSE with good ionic conductivity and stability against Li. *“The electronic and ionic conductivity of the HSE/SSE mixture will change with time due to the existing chemical reactivity between the two electrolytes, which will lead to the formation of an interphase. Understanding this interphase formation across different HSE/SSE combinations was the main aim of our study,”* states Dr. Banerjee.

To examine the interphase formation, the research team conducted several *operando* tests, i.e., they conducted the tests while the battery was in operation. Describing the experiment, Dr. Samanta says, *“We studied the formation of the interphase between the HSE and SSE using operando time-dependent impedance spectroscopy. We also analysed the interphase’s chemical composition and temperature-dependent evolution using operando synchrotron x-ray diffraction (XRD) and investigated the batteries using ex situ x-ray photoelectron spectroscopy (XPS). Finally, we conducted cycling tests to study battery life.”*

The analyses revealed that as the battery is cycled, the HSE and SSE are consumed and the interface between them changes. The interphase also increases as the reaction progresses. *“At room temperature, the reaction between the HSE and SSE will be slow, and the reaction product will be amorphous, which means it can’t be analysed using techniques like XRD,”* explains Dr. Bera. *“Temperature-dependent XRD allowed us to study the battery at temperatures up to 300°C, so we were able to identify the thermodynamically preferable phases of the electrolyte mixture.”*

The results of the XRD showed that the indium and zirconium HSEs were highly reactive and thus electrochemically incompatible with the SSE. On the other hand, the scandium, yttrium, and erbium HSEs were stable. These results were further confirmed by XPS. *“Further to this, we also conducted differential scanning calorimetry (DSC) on the electrolytes and electrolyte combinations, which further underscored these results,”* reveals Dr. Biswas.

Further expanding on this observation, Dr. Banerjee adds, *“We can explain the reactivity between the HSE and SSE using the hard–soft acid base principle (HSAB). Essentially, a highly electronegative cation—here, the central metal atom—can rapidly polarise the electron cloud around an anionic atom with a low electronegativity—here, the sulphide (S) in $\text{Li}_6\text{PS}_5\text{Cl}$, and form a covalent bond, which tends to be more reactive and less stable than an ionic bond.”*

This research marks a significant step forward in understanding the interactions between HSEs and SSEs in bilayer ASSBs. By identifying the critical role of the central metal atom in determining the chemical stability of these bilayers, the study provides a clear roadmap for the design of future ASSBs with improved stability and longer cycle life. These findings are expected to catalyse further innovations in battery technology, ultimately contributing to the development of safer, more efficient energy storage solutions essential for a sustainable future. As Dr. Banerjee rightly points out, *“Our results will guide many academics and industries to choose the correct combination of solid electrolytes, enabling commercial solid-state battery in reality.”*

We congratulate the research team on their groundbreaking work, and look forward to seeing how these insights will shape the next generation of energy storage technologies.