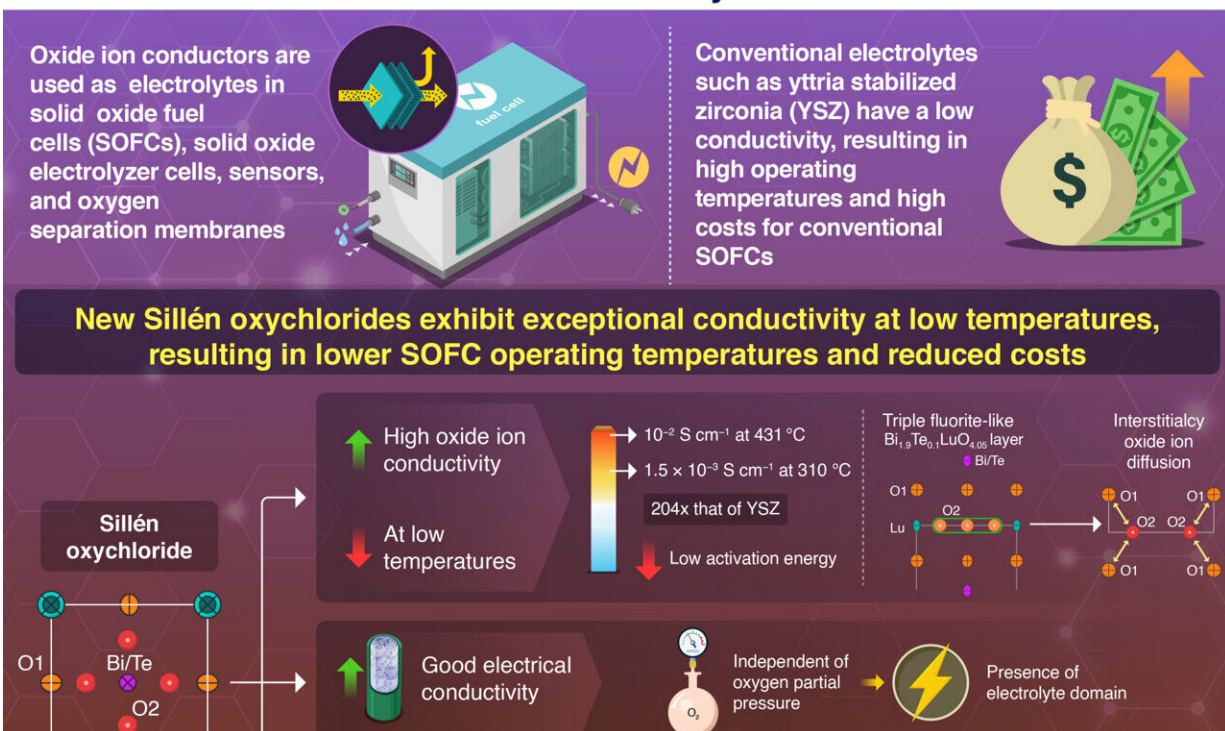


Exceptional oxide ion conductivity at lower temperatures offers potential solution for solid-state fuel cells

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Oxide Ion Conduction in Sillén Oxychlorides with Triple Fluorite-like Layers



Tokyo Tech researchers demonstrated high conductivity and stability in bismuth-containing Sillén oxyhalides with triple fluorite-like layers (e.g. 10 mS/cm at 431 °C; 204 times higher conductivity than that of conventional conductors at 310 °C). Credit: Tokyo Institute of Technology

Oxide ion conductors used in solid-state fuel cells often fail to reach full potential when operating at temperatures below 500 °C, but researchers from Tokyo Tech have recently found a solution to this problem. They demonstrated high conductivity and stability in bismuth-containing Sillén oxyhalides with triple fluorite-like layers (e.g., 10 mS/cm at 431 °C; 204 times higher conductivity than that of conventional conductors at 310 °C).

Solid oxide fuel cells (SOFCs) are known for their [high efficiency](#) and improved safety compared to other types of fuel cells. One of the key factors in SOFC performance is the [solid electrolyte](#): the oxide ion conductor. Its excellent electrochemical properties make it an ideal electrolyte not only for SOFC applications but also for solid oxide electrolyzer cells (SOECs), sensors, and oxygen separation membranes.

Despite the significant advantages of oxide ion conductors, commonly used oxide ion conductors such as yttria-stabilized zirconia (YSZ) require extremely high operating temperatures of 1000–700 °C. Over long periods, such high temperatures can be detrimental to SOFC performance. To prevent degradation, expensive heat-resistant alloys are used, which automatically increases the production cost of SOFCs. In addition, there is a lack of stable oxide ion conductors that exhibit a conductivity of $10^{-2} \text{ S cm}^{-1}$ below 500 °C.

To bridge the existing gap in the stable oxide ion electrolytes with lower operating temperatures, a team of researchers from the Tokyo Institute of Technology (Tokyo Tech), led by Professor Masatomo Yashima, recently turned their attention to Sillén oxyhalides.

In the latest *Journal of the American Chemical Society* [study](#), they synthesized a series of bismuth (Bi)-containing Sillén oxyhalides and investigated their electrical and structural properties. "We chose materials containing Bi species because they are known to exhibit high

oxide ion conductivity. Additionally, the parent materials Sillén oxyhalides possess triple fluorite-like layers with interstitial oxygen sites, which can lead to interstitialcy oxide ion diffusion," says Yashima.

In this study, the researchers synthesized Sillén oxychlorides with the molecular formula $\text{Bi}_{2-x}\text{Te}_x\text{LuO}_{4+x/2}\text{Cl}$ ($x = 0, 0.1, \text{ and } 0.2$).

The team's experiments on $\text{Bi}_{1.9}\text{Te}_{0.1}\text{LuO}_{4.05}\text{Cl}$ showed high bulk conductivity of 10 mS/cm ($= 0.01 \, \Omega^{-1} \text{ cm}^{-1}$), which is a standard for practical use in fuel cells, at a much lower temperature of 431 °C than 644 °C of the conventional material YSZ (Yttria-Stabilized Zirconia). $\text{Bi}_{1.9}\text{Te}_{0.1}\text{LuO}_{4.05}\text{Cl}$ also exhibits high bulk conductivity of $1.5 \times 10^{-3} \text{ S cm}^{-1}$ at a low temperature of 310 °C, which is more than 200 times higher than that of YSZ.

This behavior was attributed to the low activation energy. Further analysis using neutron diffraction experiments, DFT calculations, and [molecular dynamics simulations](#) revealed that the low activation energy and high conductivity emerge due to the presence of interstitialcy oxide ion diffusion in the triple fluorite-like layer of Sillén oxychlorides.

Apart from excellent oxide ion conductivity, $\text{Bi}_{1.9}\text{Te}_{0.1}\text{LuO}_{4.05}\text{Cl}$ also exhibited high electrical conductivity independent of the oxygen partial pressure at 431 °C, which indicated the presence of an electrolyte domain. It also maintained high chemical stability under CO_2 flow at 400 °C and ambient air at 600 and 400 °C.

The results of this study demonstrated that triple fluorite-like layers of Sillén oxyhalides can be used to develop high ionic conductors at temperatures below 500 °C, solving a long-standing problem with oxide ion conductors. The high ionic and [electrical conductivity](#) and chemical stability of $\text{Bi}_{1.9}\text{Te}_{0.1}\text{LuO}_{4.05}\text{Cl}$ may open new avenues for the development of superior oxide ion conductors with a triple fluorite-like

layer.

"Solid oxide fuel cells are being widely accepted as the new-age energy source, but the cost is high due to their high operating temperature. Through this research, we have developed new oxide ion conductors, which could significantly lower the [operating temperature](#) and reduce their cost," concludes Yashima.

More information: Nachi Ueno et al, High Conductivity and Diffusion Mechanism of Oxide Ions in Triple Fluorite-Like Layers of Oxyhalides, *Journal of the American Chemical Society* (2024). [DOI: 10.1021/jacs.4c00265](#)

Provided by Tokyo Institute of Technology

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