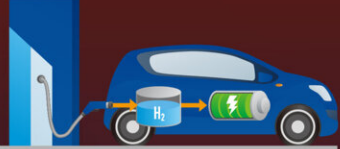


# Hexagonal perovskite oxides: Electrolytes for next-generation protonic ceramic fuel cells

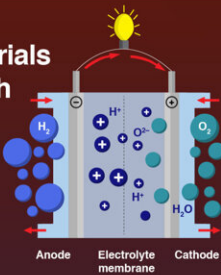
July 8 2024

## Hexagonal Perovskite-Related Oxides as Proton Conductors for Long-Lasting and Durable Fuel Cells

Protonic ceramic fuel cells (PCFCs) are an emerging type of fuel cells designed to operate at intermediate temperatures (200–500 °C) to reduce material degradation and extend their lifespan



High-performance PCFCs require materials that exhibit both high proton conductivity and high chemical stability at intermediate temperatures

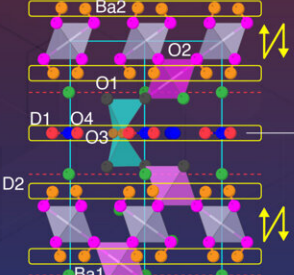


**Hydrated hexagonal perovskite-related oxides  $Ba_5R_2Al_2SnO_{13}$  as viable proton conductors ( $R = \text{rare earth Gd, Dy, Ho, Y, Er, Tm, and Yb}$ )**

$[ErO_6-SnO_6-ErO_6]$   
triple octahedral layer

$Al_2O_7$  double tetrahedral layer

$[ErO_6-SnO_6-ErO_6]$   
triple octahedral layer



Large number of oxygen vacancies at O4

O4 site is fully occupied by oxygen during hydration

- ✓ High proton conductivity of  $Ba_5Er_2Al_2SnO_{13}$  (0.01 S cm<sup>-1</sup> at 303 °C)
- ✓ High chemical

The novel hexagonal perovskite-related oxide  $Ba_5Er_2Al_2SnO_{13}$  can pave the way for the development of faster proton conductors. Credit: Tokyo Institute of Technology

Researchers from Tokyo Tech have identified hexagonal perovskite-

related  $\text{Ba}_5\text{R}_2\text{Al}_2\text{SnO}_{13}$  oxides (R = rare earth metal) as materials with exceptionally high proton conductivity and thermal stability.

Their unique crystal structure and large number of oxygen vacancies enable full hydration and high proton diffusion, making these materials ideal candidates as electrolytes for next-generation protonic ceramic fuel cells that can operate at intermediate temperatures without degradation. The study presents a significant advancement in [fuel cell technology](#).

Fuel cells offer a promising solution for [clean energy](#) by combining hydrogen and oxygen to generate electricity, with only water and heat produced as byproducts. They consist of an anode, a cathode, and an electrolyte. Hydrogen gas is introduced at the anode where it splits into protons ( $\text{H}^+$ ) and electrons.

The electrons create an electric current, while the protons migrate through the electrolyte to the cathode, where they react with oxygen to form water. Most fuel cells are solid oxide fuel cells (SOFCs), which use oxide ion conductors as electrolytes. However, a major challenge with SOFCs is the high operating temperatures required, leading to material degradation over time.

To address this, protonic ceramic fuel cells (PCFCs) that use proton-conducting [ceramic materials](#) as electrolytes are being explored. These fuel cells can operate at intermediate, more manageable temperatures of 200–500 °C. However, finding suitable materials that exhibit both high [proton conductivity](#) and chemical stability at these intermediate temperatures remains a challenge.

[In a study](#) published in the *Journal of the American Chemical Society*, researchers led by Professor Masatomo Yashima from Tokyo Institute of Technology (Tokyo Tech), in collaboration with researchers from Tohoku University, have made a significant breakthrough.

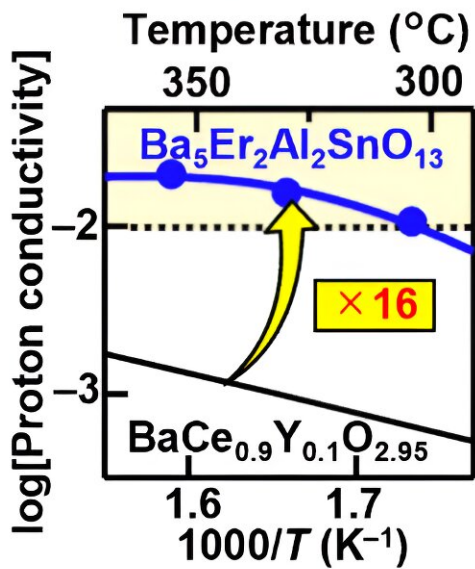
They identified chemically-stable hexagonal perovskite-related oxides  $\text{Ba}_5\text{R}_2\text{Al}_2\text{SnO}_{13}$  (where R represents rare earth metals Gd, Dy, Ho, Y, Er, Tm, and Yb) as promising electrolyte materials with a high proton conductivity of almost  $0.01 \text{ S cm}^{-1}$ , which is notably higher than that of other proton conductors around  $300 \text{ }^\circ\text{C}$ .

"In this work, we have discovered one of the highest proton conductors among ceramic proton conductors: novel hexagonal perovskite-related oxide  $\text{Ba}_5\text{Er}_2\text{Al}_2\text{SnO}_{13}$ , which would be a breakthrough for the development of fast proton conductors," says Yashima.

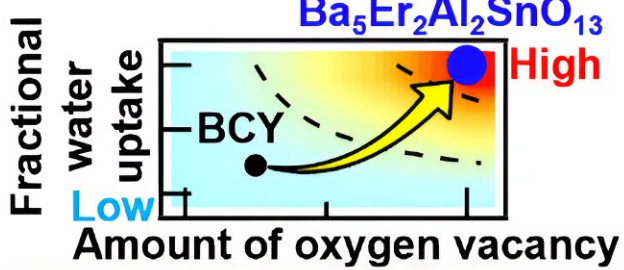
The high proton conductivity of the material is attributed to the full hydration in highly oxygen deficient material with a unique crystal structure. The structure can be visualized as a stacking of octahedral layers and oxygen-deficient hexagonal close-packed  $\text{AO}_{3-\delta}$  (h') layers (A is a large cation such as  $\text{Ba}^{2+}$  and  $\delta$  represents the amount of oxygen vacancies).

When hydrated, these vacancies are fully occupied by the oxygens from the water molecules to form [hydroxyl groups](#) ( $\text{OH}^-$ ), releasing protons ( $\text{H}^+$ ) which migrate through the structure, enhancing conductivity.

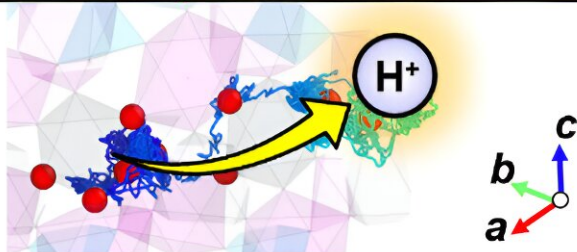
**High proton conductivity**



**High proton concentration**



**Fast proton diffusion**



Researchers from Tokyo Tech identified hexagonal perovskite-related  $\text{Ba}_5\text{R}_2\text{Al}_2\text{SnO}_{13}$  oxides (R = rare earth metal) as materials with exceptionally high proton conductivity and thermal stability. Their unique crystal structure and large number of oxygen vacancies enable full hydration and high proton diffusion, making these materials ideal candidates as electrolytes for next-generation protonic ceramic fuel cells that can operate at intermediate temperatures without degradation. Credit: Professor Masatomo Yashima

In their study, the researchers synthesized  $\text{Ba}_5\text{Er}_2\text{Al}_2\text{SnO}_{13}$  (BEAS) using solid-state reactions. The material had a large amount of oxygen vacancies ( $\delta = 0.2$ ) and exhibited a fractional water uptake of 1, indicating its capacity for full hydration. When tested, its conductivity in a wet nitrogen environment was found to be 2,100 times higher than in a dry nitrogen environment at 356 °C. When fully hydrated, it achieved a conductivity of  $0.01 \text{ S cm}^{-1}$  at 303 °C.

Moreover, the arrangement of atoms in the octahedral layers provides

paths for proton migration, further increasing proton conductivity. In simulations of  $\text{Ba}_5\text{Er}_2\text{Al}_2\text{SnO}_{13}\cdot\text{H}_2\text{O}$ , the researchers studied proton movement in a  $2\times 2\times 1$  supercell of the crystal structure, represented by  $\text{Ba}_{40}\text{Er}_{16}\text{Al}_{16}\text{Sn}_8\text{O}_{112}\text{H}_{16}$ . This structure included two h' layers and two octahedral layers. The researchers found that protons in the octahedral layer showed long-range migrations of protons, indicating fast proton diffusion.

"The high proton conductivity of BEAS is attributed to its high proton concentration and diffusion coefficient," explains Yashima.

In addition to its high conductivity, the material is also chemically stable at the operating temperatures of PCFCs. Upon annealing the material under wet atmospheres of oxygen, air, hydrogen, and  $\text{CO}_2$  at  $600\text{ }^\circ\text{C}$ , the researchers observed no changes in its composition and structure, indicating the material's robust stability and suitability for continuous operation without degradation.

"These findings open new avenues for proton conductors. The high proton conductivity via full hydration and fast proton migration in octahedral layers in highly oxygen-deficient hexagonal perovskite-related materials would be an effective strategy for developing next-generation proton conductors," says Yashima. With its exceptional properties, this material could lead to efficient, durable, and lower-temperature fuel cells.

**More information:** Kohei Matsuzaki et al, High Proton Conduction in the Octahedral Layers of Fully Hydrated Hexagonal Perovskite-Related Oxides, *Journal of the American Chemical Society* (2024). [DOI: 10.1021/jacs.4c04325](https://doi.org/10.1021/jacs.4c04325)

Provided by Tokyo Institute of Technology

Citation: Hexagonal perovskite oxides: Electrolytes for next-generation protonic ceramic fuel cells (2024, July 8) retrieved 8 July 2024 from <https://techxplore.com/news/2024-07-hexagonal-perovskite-oxides-electrolytes-generation.html>

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