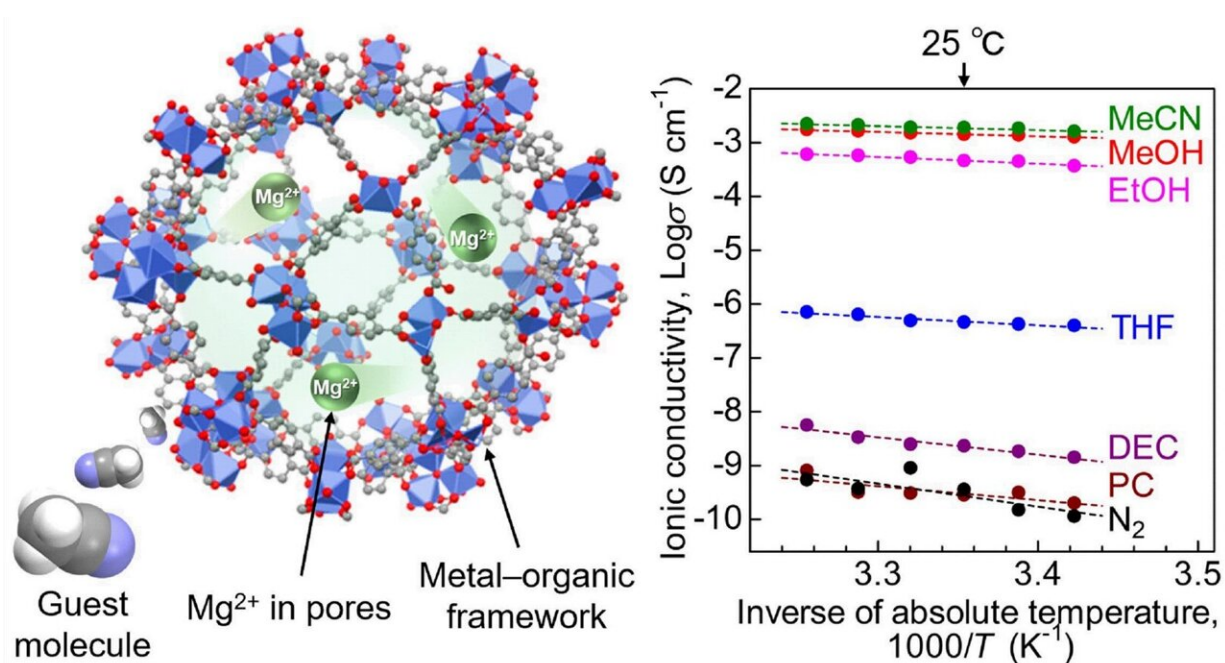


New magnesium superionic conductor for lithium-free solid-state batteries

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The new Mg^{2+} conductor consists of a metal–organic framework holding Mg^{2+} ions in its pores. A “guest molecule” acetonitrile is introduced into the structure to accelerate the ionic conductivity of Mg^{2+} and allow its migration through the solid. Credit: Masaaki Sadakiyo from Tokyo University of Science

The development of highly efficient energy storage devices that can store renewable energy is crucial to a sustainable future. In today's world, solid-state rechargeable lithium ion (Li^+) batteries are the state of the art. But lithium is a rare earth metal, and society's dependence on the

element is likely to lead to a rapid decline in resources and subsequent price hikes.

Magnesium ion (Mg^{2+})-based batteries have gained momentum as an alternative to Li^+ . The earth's crust holds ample magnesium, and Mg^{2+} -based energy devices are said to have high energy densities, high safety, and low cost. But the wide application of Mg^{2+} is limited by its poor [conductivity](#) in solids at room temperature. Mg^{2+} has poor solid-state conductivity because divalent positive ions (2+) experience strong interactions with their neighboring negative ions in a solid crystal, impeding their migration through the material.

This hurdle was recently overcome by a research team from the Tokyo University of Science (TUS). In their new study published online on 4 May 2022 and on 18 May 2022 in volume 144 issue 19 of the *Journal of the American Chemical Society*, they report for the first time, a solid-state Mg^{2+} conductor with superionic conductivity of $10^{-3} \text{ S cm}^{-1}$ (the threshold for practical application in solid-state batteries). This magnitude of conductivity for Mg^{2+} conductors is the highest reported to date. According to Junior Associate Professor Masaaki Sadakiyo of TUS, who led the study, "In this work, we exploited a class of materials called metal–organic frameworks (MOFs). MOFs have highly porous crystal structures, which provide the space for efficient migration of the included ions. Here, we additionally introduced a 'guest molecule,' acetonitrile, into the pores of the MOF, which succeeded in strongly accelerating the conductivity of Mg^{2+} ." The research group further included Mr. Yuto Yoshida, also from TUS, Professor Teppei Yamada from The University of Tokyo, and Assistant Professor Takashi Toyao and Professor Ken-ichi Shimizu from Hokkaido University. The paper was made available online on May 4, 2022 and was published in Volume 144 Issue 19 of the journal on May 18, 2022

The team used a MOF known as MIL-101 as the main framework and

then encapsulated Mg^{2+} ions in its nanopores. In the resultant MOF-based electrolyte, Mg^{2+} was loosely packed, thereby allowing the migration of divalent Mg^{2+} ions. To further enhance ion conductivity, the research team exposed the electrolyte to acetonitrile vapors, which were adsorbed by the MOF as guest molecules.

The team then subjected the prepared samples to an alternating current (AC) impedance test to measure ionic conductivity. They found that the Mg^{2+} electrolyte exhibited a superionic conductivity of $1.9 \times 10^{-3} \text{ S cm}^{-1}$. This is the highest ever reported conductivity for a crystalline solid containing Mg^{2+} .

To understand the mechanism behind this high conductivity, the researchers carried out infrared spectroscopic and adsorption isotherm measurements on the electrolyte. The tests revealed that the acetonitrile molecules adsorbed in the framework allowed for the efficient migration of the Mg^{2+} ions through the body of the solid electrolyte.

These findings of this study not only reveal the novel MOF-based Mg^{2+} conductor as a suitable material for battery applications, but also provide critical insights into the development of future solid-state batteries. "For a long time, people have believed that divalent or higher valency ions cannot be efficiently transferred through a solid. In this study, we have demonstrated that if the crystal structure and surrounding environment are well-designed, then a solid-state high-conductivity conductor is well within research," explains Dr. Sadakiyo.

When asked about the research group's future plans, he reveals that they "hope to further contribute to society by developing a divalent conductor with even higher ionic conductivity."

More information: Yuto Yoshida et al, Super Mg^{2+} Conductivity around $10^{-3} \text{ S cm}^{-1}$ Observed in a Porous Metal–Organic Framework,

Journal of the American Chemical Society (2022). [DOI: 10.1021/jacs.2c01612](https://doi.org/10.1021/jacs.2c01612)

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