New data gained on double perovskite oxides

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The Journal of Alloys and Compounds has published an article coauthored by the Institute of Solid State Chemistry and Mechanochemistry (the Ural Branch of the Russian Academy of Sciences), the Donostia International Physics Centre, and the HSE Tikhonov Moscow Institute of Electronics and Mathematics on the characteristics of cubic double perovskite oxides. To date, experimental measurements of the minerals' characteristics have not corresponded to the results of theoretical modeling. The work marks the first time that researchers have set themselves the task of explaining this disparity. The data obtained will allow researchers to improve low-temperature fuel cell technologies—one of the main alternatives to current sources of electricity.

There is growing support among researchers for the use of fuel cells instead of more widely known galvanic batteries. Typical batteries contain limited amounts of substances used to generate electricity—once the battery runs out of fuel, it stops working. In fuel cells, hydrogen fuel mixes with oxygen to generate electricity, heat, and water, with the fuel being fed from outside and oxygen taken from the air. This means that such batteries can operate as long as they have a stable power supply. The only byproduct of the process is water, which makes the cells an environmentally friendly alternative to manganese or zinc-based batteries, which must be disposed of at the end of their life.

Solid oxide fuel cells (SOFCs) are an increasingly promising technology. The cells use a ceramic material (such as zirconium dioxide) as an electrolyte—a medium between positively and negatively charged

electrodes. Advantages of solid oxide fuel cells include high efficiency, reliability, the ability to be powered by different kinds of fuel, and a relatively low cost.

Moreover, unlike other types of fuel cells, SOFCs do not necessarily need to be flat with an electrolyte between electrodes. They can take different forms, such as tubes through which air or fuel flows through the inner side, with another gas flowing along the outer side.

Solid oxide fuel cells also have one main disadvantage: They require high temperatures (around 500–1000°C) to sustain the necessary chemical reactions. Expensive platinum catalysts are required to use SOFCs at lower temperatures, which increases the cost of fuel cells immensely.

For this reason, many researchers have been looking for ways to decrease the operating temperatures of solid oxide fuel cells without compromising the efficiency of their electricity generation. Areas of research in the field include searching for highly active catalysts for the required reactions, the development of techniques to synthesize SOFC components, and the creation of effective materials for electrodes.

Researchers have proposed using perovskite-like minerals as electrolytes with the required properties for industrial application. Perovskites are a class of minerals composed of two negatively charged ions and one positively charged ion attached to one another. The authors proposed using complex oxide of molybdates with the double perovskite structure A_2MeMoO_6, where A represents calcium, strontium, or barium, and Me represents 3d metals or magnesium.

Compositions in which A = strontium and Me = magnesium or nickel have been identified as the most promising. These oxides exhibit good electrical conductivity under reducing conditions, as well as a tolerance

to sulfur and carbon oxide impurities in fuel gas.

Despite their appeal from a practical viewpoint, the properties of double perovskite-like molybdenum oxides such as $Sr_2Mg_{1-x}Ni_xMoO_6$ are not fully understood. Experimental measurements of the substances' properties differ from theoretical predictions derived from computational modeling, which are themselves highly dependent on initial assumptions and the software code used.

The authors of the article have made the first attempt to combine computer modeling of the substance's electronic spectrum with experimental data of how $Sr_2Mg_{1-x}Ni_xMoO_6$ conducts electric current. The results support the semiconducting nature of $Sr_2Mg_{1-x}NixMoO_6$ conductivity. As in metals, the motion of charged particles in semiconductors generates an electrical current. However, in metals, the presence of free electrons is due to the structure of the substance and the electron bonds in atoms, while the presence of charge carriers in semiconductors is determined by numerous factors, the most important of which are the purity and temperature of the semiconductor.

The researchers agree that semiconductors can be effectively used as electrolytes in fuel cells thanks to their good electrochemical characteristics and high ion conductivity. They believe that further studies of double perovskite-like oxides will offer new opportunities to use this promising material in various energy technologies.

More information: K.S. Tolstov et al, The impact of atomic defects on high-temperature stability and electron transport properties in $Sr_2Mg_{1-x}Ni_xMoO_{6-\delta}$ solid solutions, *Journal of Alloys and Compounds* (2021). DOI: 10.1016/j.jallcom.2021.160821