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Editorial

Towards Perovskite Oxide-Based Electrocatalysts with Zero-Critical Elements for Sustainable Energy Production

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The well-being of the Earth and its inhabitants is compromised by the energy and climate crisis that has arisen from the prolonged and uncontrolled utilization of fossil fuels, which has caused a tremendous increase in anthropogenic CO_2 and a consistent depletion of natural energy resources. This point of no return forces us as scientists to face the biggest green energy transition in world history, based on multiple effective strategies for clean and renewable energy production with zero-CO_2 emissions [1,2]. The development of solid oxide fuel cell (SOFC) technologies constitutes a piece of the clean energy transition puzzle thanks to their efficiency and the possibility of coupling them with co-electrolysis for CO_2 recycling [3,4]. At large scale, SOFC stacks can supply gigawatts of electricity for utilization, although a long-term vision must consider the present and future availability of the raw materials required for producing each component of SOFCs [5,6].

Periodically, the European Commission (EU) compiles a list of critical raw materials (CRMs) based on economic, political, and social factors. The last update drawn up by the EU dates back to 2023; in the same year, the U.S. government also released its list of critical materials [7,8]. The governmental reports represent tools that researchers should use for sustainable material development. In addition, the EuChemS periodic table of elements is also a useful tool that classifies elements based on the concepts of "availability", "sustainability", and "overuse" [9].

In this context, the development of materials for SOFC components must not fail to take into consideration the critical elements issue, and it needs to move towards zero- or low-critical element contents. Herein, the attention is focused on perovskite oxide-based electrodes for SOFCs working at intermediate temperatures (IT-SOFCs), namely between 600 and 800 °C.

With the general formula ABO_3, perovskite oxides have been widely explored as electrocatalysts for SOFCs thanks to their versatility in promoting both oxygen reduction reactions (ORRs) at the cathode and fuel oxidation reactions at the anode. Many studies have dealt with doping strategies both at A- and B-sites, aiming to improve electrochemical properties. Below 800 °C, i.e., at intermediate temperatures, $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ (LSCF) plays a key role as an air electrode, exhibiting high mixed ionic–electronic conductivity and electrocatalytic activity for ORRs, although a lack of performance is due to thermal expansion coefficient mismatch with electrolytes or Gd- or Sm-doped ceria [10,11]. Even $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (BSCF) is considered a good cathode material mainly thanks to its high oxygen permeability [10,11].

Unfortunately, lanthanum, strontium, and cobalt—the most used elements in the investigated perovskite oxide-based compositions—are critical [7,8], but studies about perovskite oxide-based cathodes containing low- and/or zero-critical elements are gradually increasing in volume. Most articles treat Co-free perovskites mainly using Fe as a substitute, whereas Sr is generally replaced by alkaline earth metals [12–14]. Ca- and Ba-doped $LaFeO_3$ perovskite oxides have recently been investigated as cathodes for IT-SOFC in comparison with $La_{0.6}Sr_{0.4}FeO_3$. In a single-cell configuration, Sr-doping has a major positive influence

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on electrochemical performance, and Ca- and Ba-doping offer results that bode well for the future substitution of Sr but not of La [12]. Another strategy to mitigate the use of critical metals consists of the introduction of a reduced amount of critical elements, with positive effects, as in the case of $Pr_{0.5}Ba_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$, where Pr and Cu are critical metals [13]. Moving in this direction, more complex cases are high-entropy perovskite oxides like $La_{0.2}Pr_{0.2}Sm_{0.2}Nd_{0.2}Sr_{0.2}FeO_{3-\delta}$, which, in a single-cell configuration, exhibit prolonged durability at 700 °C [14]. Even if Pr, Nd, and Sm are also critical like Sr and La, the advantages in electrochemical performance due to the higher configurational entropy promoted by the presence of several critical elements in small amounts can be utilized as a way to avoid the massive exploitation of a single critical element in the same material.

In general, it is difficult to maintain good levels of performance with zero-critical element contents in perovskite oxide-based electrocatalysts, and this issue concerns cathode materials as well as anode materials since most of the metals responsible for the electrocatalytic activity towards fuels are considered critical. Over the years, Ni-based cermets have been shown to be the most competitive materials despite electrocatalyst inactivation due to carbon deposition in carbon-rich fuels; however, Ni is listed as critical [7,8,15]. Thus, perovskite oxide-based anodes represent a sustainable challenge that deserves to be faced. Conversely, doped $La_{1-x}Sr_xCrO_3$ and doped $SrTiO_3$ have been widely investigated with good electrochemical performance with H_2- and/or CH_4-based fuels [15]. In addition, doped $LaFeO_3$, like Mo-doped $La_{0.6}Sr_{0.4}(Co_{0.2}Fe_{0.8})_{1-x}Mo_xO_{3-\delta}$, has been studied for the oxidation of methane, biogas, and methanol [16].

Finally, two important questions emerge from these considerations: (1) How can society move towards sustainable energy using perovskite-based electrocatalysts with a low content of critical elements, whose presence is still needed to reach high levels of efficiency? (2) Is it sustainable to develop materials for renewable energy with zero- or low-critical elements only from natural resources? While looking for reasonable answers, it is urgent to explore new compositions considering the lists of critical materials and, at the same time, to assess technologies that recover from scraps and waste all those critical elements that ensure competitive performance (Figure 1). For perovskite oxide-based electrocatalysts, the game is still open for play, and the outcomes are all in our hands.

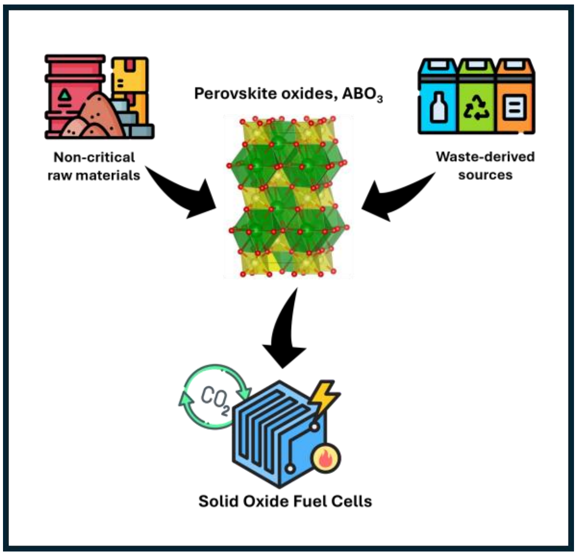

Figure 1. Perovskite oxide electrocatalysts for sustainable energy production are obtained from non-critical raw materials and/or from waste-derived sources. (Perovskite oxide image realized using VESTA version 3).

Conflicts of Interest: The authors declare no conflicts of interest.

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