

# Microwave-Triggered Redox Switching of Materials Enables Hydrogen Production and Green Chemistry

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## 1 Introduction

The path towards a sustainable future requires an urgent action on our climate impact by relying on renewable energy and eliminating fossil fuels from industry and transport. The use of CO<sub>2</sub>-neutral carriers or chemical raw materials produced by electricity coming from solar parks and wind farms is expected to significantly limit greenhouse gas emissions [1]. However, the higher affordability of renewables is still accompanied by their volatile nature, posing the challenge of efficient energy storage methods, together with novel techniques to electrify unitary steps in process industry [2].

In this context, hydrogen has a promising potential as an energy storage medium, both with the purpose of covering the demand for energy in the periods of lower availability of renewable energy, or for being directly employed in chemical processing.

Most of the world's current hydrogen production relies on a CO<sub>2</sub> intensive process called Steam Methane Reforming, but it can also be produced by water electrolysis with a resulting zero-carbon footprint, being known as green hydrogen. An attractive variant of this method is the thermochemical water splitting (TCWS) approach [3], consisting of two steps: first, a metal oxide is heated and reduced to form oxygen vacancies and release oxygen; second, water is dissociated by re-oxidation of the metal oxide thus releasing the hydrogen. This process creates a close loop in which the metal oxide remains intact after the cycle, and only water and heat are consumed. This redox process currently requires very high-temperature heating, such as the recently reported application of concentrated solar energy, involving extreme process conditions and solar setups of high complexity [4].

The growing demand for green hydrogen sources has pushed the limits of technology towards new cost-efficient alternatives [1]. Electromagnetic energy appears as one of these alternatives, having proven to be very efficient in activating chemical reactions [5]. In particular, microwave technology offers multiple advantages for electrochemical operation including non-contact processes and less constraints and complexity than conventional electrolysis cells.

An example of production of green hydrogen using microwaves has recently been published [6] with notable technological relevance. The process employs microwave energy to reduce the metal oxide prior to water vapor splitting and operates in a simple reactor at substantially lower temperatures (below 250°C) than those required with other technologies (1000-1500°C) [4].

## 2 Microwave-induced reduction

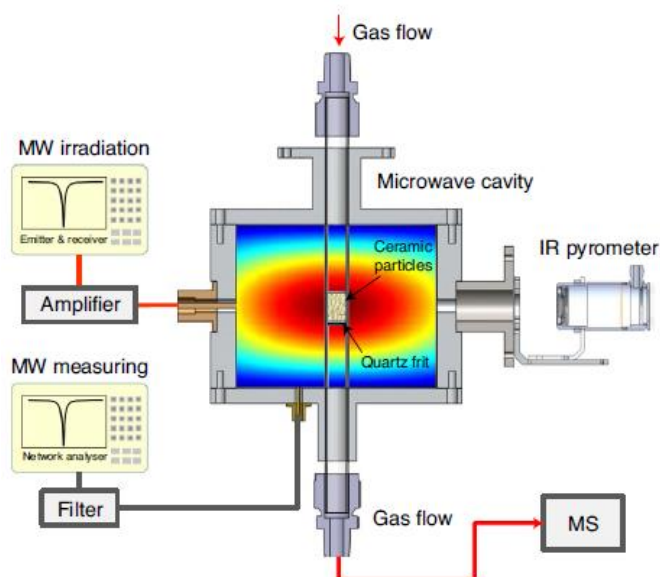


Figure 1: Microwave equipment employed in the study. Figure from [6].

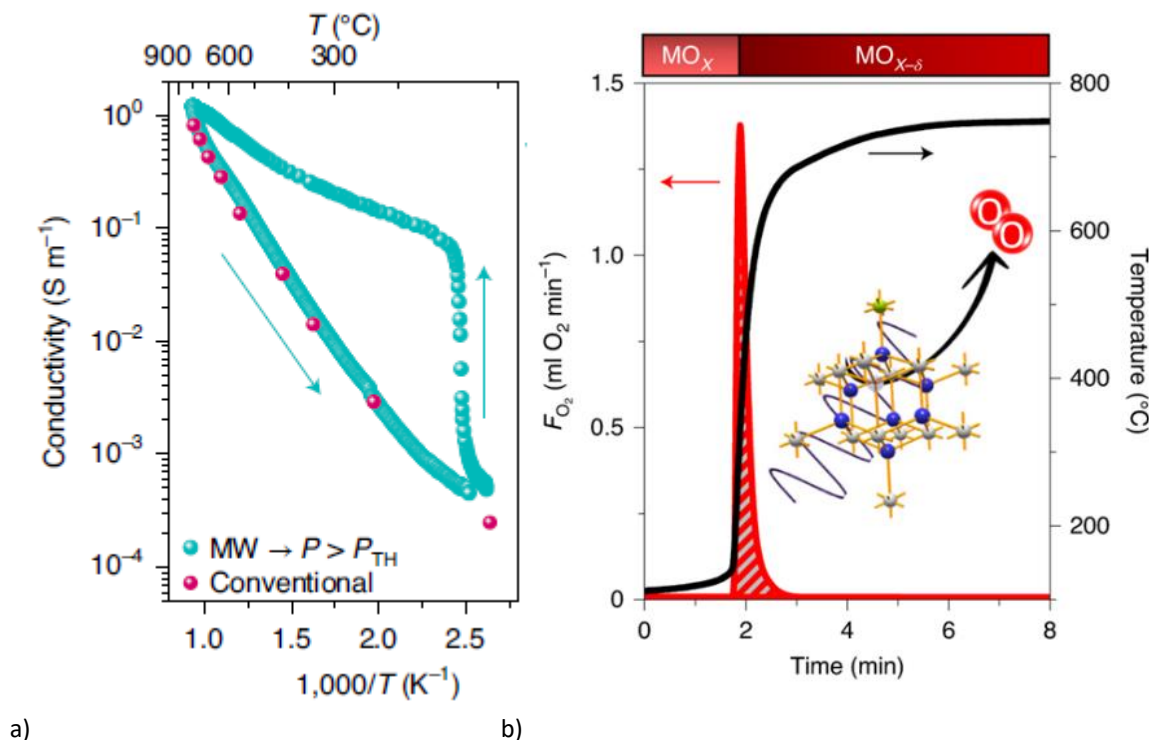
The microwave energy was applied in a dual-mode microwave cylindrical cavity capable to heat by microwaves and simultaneously measure the a.c. conductivity of material samples up to 1000°C (Figure 1). This dual-mode cavity and associated equipment was developed in 2015 to investigate the temperature-dependent dielectric properties of materials under intense microwave fields and since then it has been widely employed in numerous studies that have confirmed it as a relevant equipment to identify the mechanisms behind microwave and matter interactions, including unprecedented reaction pathways [7].

In this specific application, the sample was placed in a quartz holder modified to operate under continuous flow conditions and different gas atmospheres. The microwave system included a mass spectrometer for in situ off-gas analysis, videocamera for image recording and infrared pyrometer for temperature measurements. Since the temperature of the sample was determined from surface IR measurements and temperature gradients were expected in the sample due to the typical inverted temperature profile in microwave-heated samples, a thorough calibration procedure was

applied to obtain the average bulk temperature of the sample. This calibration procedure included, among others, optical fiber measurements and Raman spectrometry of reference materials [8].

In order to illustrate the microwave redox principle, a doped ceria metal oxide CGO ( $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ ) was selected, as ceria is a well-known ion-conductor, showing other advantages such as large oxygen storage capacity and high oxide-ion diffusivity. Samples of CGO were employed because of its structural stability, combined with a large amount of oxygen vacancies leading to a great reductive power.

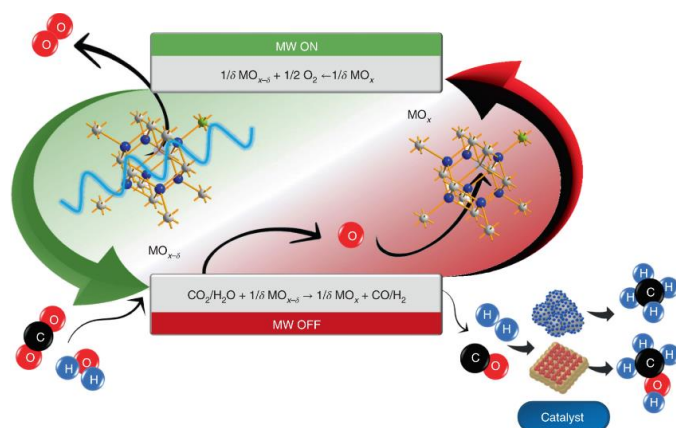
The effect of CGO reduction under microwave irradiation, and the differences respect to conventional heating were investigated through contact-less determination of its a.c. conductivity. Figure 2 shows this comparison, illustrating the typical Arrhenian behaviour under conventional heating (with predominant oxide-ion conduction) [9]. However, microwave heating lead to a very different conductivity profile, with a steep increase at a relatively low temperature ( $\sim 150^\circ\text{C}$ ) followed by a temperature range with different activation energy.



**Figure 2:** a) Measurements of CGO a.c. conductivity under microwave and conventional heating. b) Off-gas analysis during microwave cycle showing oxygen release. Figures from [6].

In situ off-gas analysis revealed an abrupt release of oxygen simultaneous to the sharp increase of conductivity (Figure 2), in contrast to a negligible oxygen release under conventional heating. It should be noted that a considerable amount of oxygen  $>0.2\text{mL}$  per gram of CGO was released for a threshold microwave power of  $P_{\text{TH}} \sim 10\text{Wg}^{-1}$ . This indicated a partial reduction of ceria atoms ( $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ ) induced by microwave energy with the formation of localized electronic charge carriers (polarons) and oxygen vacancies. The increasing population of electronic carriers combined with their high mobility at these temperatures ( $170\text{--}350^\circ\text{C}$ ) contributed in turn to a drastic enhancement of electronic conductivity (n-type). Close to the complete  $\text{O}_2$  release, the residual increase of conductivity could be attributed to the thermal mobility of both oxygen vacancies and electrons, changing gradually from electronic to an oxide-ion transport-dominated conductivity. During the cooling cycle, the conductivity followed the conventional path, since electronic mobility was not activated due to the absence of microwave energy.

The way that microwave energy modified the CGO lattice structure and electronic configuration was also studied through X-ray photoelectron spectroscopy of activated CGO, showing oxygen vacancies and a  $\text{Ce}^{3+}/\text{Ce}^{4+}$  surface ratio of approx. 27% [6].



**Figure 3:** Diagram of the complete microwave redox cycle yielding different products with proper selection of the low-energy molecules present in the re-oxidation step. Figure from [6].

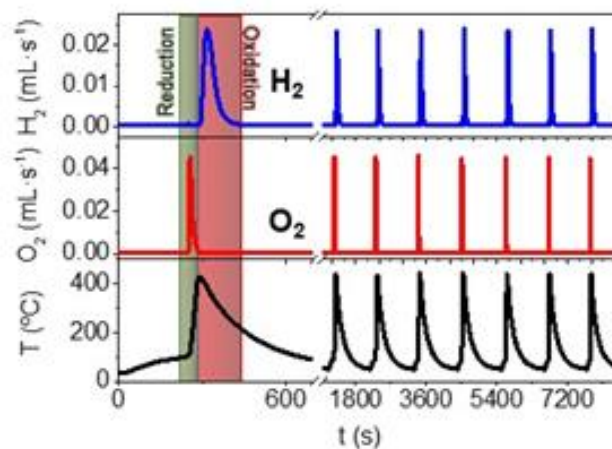
Once the CGO sample has been activated by microwave energy, it tends to re-oxidize by reacting with other low-energy molecules, such as water,

capturing the oxygen and releasing the hydrogen. The adequate selection of the gases present during the re-oxidation step allows producing other valuable products, extending the benefits to other reactions such as intensified hydrocarbons synthesis (Figure 3).

### 3 Hydrogen production with microwaves

The complete sequence for hydrogen generation was demonstrated with CGO in a wet atmosphere ( $\text{N}_2$  atmosphere with 3% water) (see Figure 4). The applied microwave power (from 10 to  $40\text{Wg}^{-1}$ ) induced the oxygen release (this oxygen was evacuated) and maintained the sample in the reduced state (at a temperature below  $400^\circ\text{C}$ ). When microwaves were no longer applied, the activation effect disappeared giving way to a rapid re-oxidation of CGO with the oxygen provided by water molecules, thus releasing the hydrogen and completing the loop.

Results showed that this loop could be repeated in a stable and cyclable process with excellent reproducibility, paving the way for the hydrogen production through different configurations, such as microwave-swing reactors or chemical looping schemes [10]. The thermodynamic analysis and an estimation of the hydrogen production cost through microwave redox showed promising results, which could be competitive with conventional water electrolysis technologies.



**Figure 4:** Consecutive cycles of microwave-driven CGO reduction and oxidation in a wet atmosphere to release hydrogen revealed the good stability and reproducibility of the process. Figure from [6].

## 4 Conclusions

Microwave-driven electrochemical reactions such as water electrolysis can be performed with this technique allowing non-contact activation without the restrictions imposed by the operation of electrolytes or electrodes (temperature, pressure, challenging electric contacting, etc.).

The wide range of possible applications is even expanded with the integration of the adequate synthesis catalysts. Simultaneous microwave deoxygenation of water and CO<sub>2</sub> could enable syngas production for the synthesis of added-value chemicals, or the production of different hydrocarbons, as the reported CH<sub>4</sub> employing a Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-catalyst.

Apart from microwave electrocatalysis, further work on materials formulation and refined microwave engineering could maximize the energy efficiency (electric work and enthalpies of reduction and re-oxidation) facilitating the application of this technology in other diverse areas. Energy storage is an attractive example, where future uses include ultrafast battery charge through microwave volumetric reduction of anode-chamber materials.

## For further readings

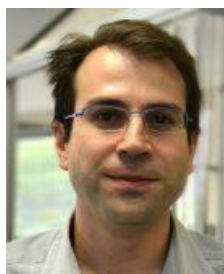
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## About the authors



**Beatriz García-Baños** was born in Madrid, Spain, in 1979. She received the B.S., M.S., and Ph.D. degrees in communications from the Universidad Politécnica de Valencia, Spain, in 2003, 2005, and 2008, respectively. From 2003 to 2008, she was a Research Assistant with the Universidad Politécnica de Valencia. In 2008, she joined the Microwaves Industrial

Applications Division (DIMAS), Institute for the Applications of Advanced Information and Communication Technologies (ITACA), where she is specialized in developing microwave equipment for dielectric characterization, materials and process monitoring, and heating processes. She has authored or coauthored more than 40 articles and conference proceedings. She is the author of the book: *Study and Optimization of Microwave Sensors for Characterization and Monitoring of Materials in Industrial Processes* (Madrid, Spain: ProQuest Dissertations & Thesis, 2009). She holds 4 patents. Her current research interests include microwave sensors and systems for materials characterization, microwave monitoring of industrial processes, and microwave heating devices.



**José M. Serra** (1976) did his Ph.D. work at the Institute of Chemical Technology (ITQ) directed by Prof. A. Corma in collaboration with the Institute Français du Pétrole. He leads the Energy Conversion and Storage Group, the Fuel Cells and Ionic Membranes research line. The current activities are principally focused on the application

of catalysis and materials science in: (a) the development of solid oxide fuel cells components; and (b) development of mixed ionic-electronic conducting membranes for oxygen and hydrogen separation and catalytic membrane reactor applications. He is co-author of more than 165 scientific articles, 15 book chapters, and 25 patents in the field of catalysis and energy. Prof. Serra is the CSIC representative for the European Energy Research Alliance (EERA): Basic Science for Energy Joint Programme (AMPEA), Deputy Coordinator of the subprogram Materials Science in AMPEA. For his

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**José M. Catalá-Civera** (M'04–SM'15) was born in Valencia, Spain, in 1969. He received the Dipl.Ing. and Ph.D. degrees from the Universitat Politècnica de València, Valencia, in 1993 and 2000, respectively. Since 1996, he has been with the Communications Department, Universitat Politècnica de València,

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Director of the Institute. His current research interests include the design and application of microwave theory and applications, the use of microwaves for electromagnetic heating, microwave cavities and resonators, measurement of dielectric and magnetic properties of materials, and development of microwave sensors for nondestructive testing. He has published over 100 peer-reviewed articles in refereed journals and conference proceedings and received research funding from various sources including awards from the European Union programs (EU), National Institute of Standards and Technology (NIST) and industry contracts. He is also a holder of 24 national and international patents. Prof. Catalá-Civera is reviewer of several international journals, IEEE Senior Member and participates in several international professional and scientific associations. He was General Chair of 2019 International Conference on Microwave and High Frequency Heating organized by the Association of Microwave Power in Europe for Research and Education (AMPERE), a European-based organization devoted to the promotion of RF and microwave energy.

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## ***Microwave Pre-Treatment of Recalcitrant Dairy Waste for Anaerobic Digestion***

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### **1 Introduction**

Ireland has a strong dairy industry, expanding in recent years after the abolition of the EU milk quota in 2015 [1]. The subsequent increase in dairy production along with growing interest in the circular economy as a means to mitigate climate change and biodiversity loss have led to an urgency in efforts to reduce the environmental impact of the industry. For every liter of milk produced, 3 L of dairy wastewater are generated which must be treated before discharge to water bodies. Dairy processing wastewater comes from tank washings, waste products at various stages of production, and spoiled milk. The wastewater contains considerable concentrations of fats, oils, and greases (FOGs), non-soluble in the wastewater. FOGs are composed of

highly recalcitrant compounds which are difficult to treat and are inhibitory to the microbial community in the biofilms of anaerobic digesters. While the aqueous phase of dairy wastewater may be treated by aerobic means and anaerobic digestion (AD) to generate biomethane, the FOG fraction must be removed.

FOGs are separated from the dairy wastewater stream by a process called dissolved air flotation (DAF). Briefly, compressed air is pumped into the bottom of the DAF tank. Air bubbles expand as they rise, floating the immiscible FOGs to the surface. Beams skim the surface of the DAF tank, sweeping the FOG sludge into a collection tank, while the remaining water is pumped to further treatment. Flocculant and polymeric coagulant may be added to