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Electromagnetic simulation studies of microwave assisted heating for the processing of nanostructured iron oxide for solar driven water splitting

S. Saremi-Yarahmadi[a,*], W. Whittow[b], B. Vaidhyanathan[a]

[a] Department of Materials, Loughborough University, Loughborough, LE11 3TU, UK
[b] School of Electronic, Electrical and Systems Engineering, Loughborough University, Loughborough, LE11 3TU, UK

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ABSTRACT

Microwave assisted preparation has been shown to improve the performance of hematite photoelectrodes for solar driven water splitting. To understand the microwave heating process further, the distribution of the electromagnetic (EM) fields within the material is analysed using finite-difference time-domain (FDTD) EM software. The rate of the increase in temperature is calculated from the simulated EM field distributions. In order to validate the simulation results, the calculated temperatures were compared with the experimental temperatures obtained using a thermal imaging camera.

1. Introduction

Generation of hydrogen through photoelectrochemcial (PEC) water splitting is one of the most promising alternatives for the production of hydrogen as a fuel. In this method, light is absorbed by a semiconductor electrode which then provides the energy required to break water molecules into hydrogen and oxygen. So far a variety of semiconductor materials such as TiO_2 [1–3], $SrTiO_3$ [4], CdS [5,6], WO_3 [7,8] and Fe_2O_3 [9,10] has been used as PEC water splitting photoelectrodes. The desirable material capable of driving the reactions involved in the photocatalysis of water is required to satisfy several requirements; suitable bandgap, favourable positioning of the band edge energy levels, stability in aqueous environment, abundance and ease of fabrication are considered to be the most important [11–13].

Hematite (α-Fe_2O_3) is a strong candidate photoelectrode for PEC water splitting as it meets most of the selection criteria of a suitable material for this application such as bandgap, chemical and PEC stability, and ease of fabrication [14–16]. However, one of the major barriers in the development of efficient hematite photoelectrodes is the short hole diffusion length in hematite (2–4 nm) hence poor hole transport at the hematite/electrolyte interface [17,18]. As a result, photocurrent densities and conversion efficiencies reported for undoped hematite electrodes have not been promising.

Microwave irradiation has shown great potential for the processing of different inorganic solids [19]. The use of microwave irradiation in processing of materials has been shown to offer several advantages such as shorter synthesis time, higher yields, better particle shape control and chemical plant size reduction [20–22]. Recently, we reported a facile microwave assisted route for the fabrication of iron oxide photoelectrodes which showed improved PEC performance [16,23]. We showed for the first time that the conversion of iron into iron oxide using a microwave assisted process occurred at lower temperatures and at faster times than what had been previously reported [16]. It was also demonstrated that the less demanding processing conditions associated with the microwave approach combined with the specific advantage of rapid heating and cooling. The performance of microwave-prepared films surpassed that of the samples annealed conventionally while a total energy savings of >60% was achieved [16]. For example, as shown in Fig. 1, the highest photocurrent density at 0.55 V vs. $V_{Ag/AgCl}$, before the dark current onset, was ~400 $\mu A\,cm^{-2}$ for the films annealed at 250 °C for 15 min using microwave irradiation while conventional annealing at the same temperature resulted in samples with negligible (3 $\mu A\,cm^{-2}$) photoactivity [16].

In order to understand the specific role played by microwave we examined the effect of microwave power on the performance of nanostructured hematite photoelectrodes using hybrid heating [23]. This study confirmed the genuine and effective role of the microwave energy in improving the photo-performance of hematite electrodes; the photo-performance increased as more microwave power was applied at the same temperature-time profiles (Fig. 1 inset). The effectiveness of the role of microwave heating

* Corresponding author. Tel.: +44 1509 223168; fax: +44 1509 223949.
E-mail address: S.Saremi@lboro.ac.uk (S. Saremi-Yarahmadi).

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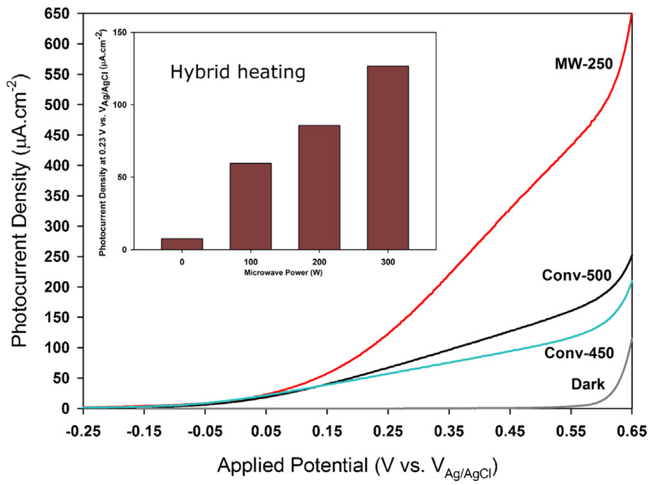

Fig. 1. Graph showing the photocurrent density vs. applied potential for the undoped samples annealed using conventional (Conv) and microwave heating (MW). Samples were annealed for 15 min at 250, 450 and 500 °C [16]. Inset) The bar chart showing the linear increase of the photocurrent density at 0.23 V vs. $V_{Ag/AgCl}$ of hematite photoelectrodes (heated at 500 °C for 30 min) as a function of microwave power applied in hybrid heating [23].

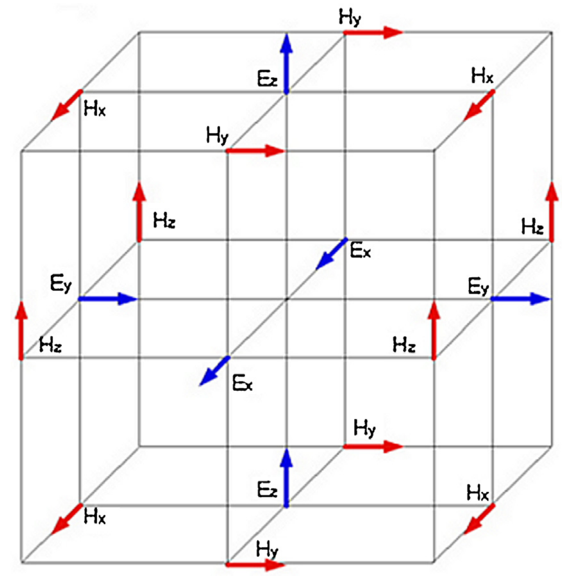

Fig. 2. The Yee cell with six Cartesian electric (*E*) and magnetic field (*H*) components.

in improving the photo-performance (i.e. higher photocurrent density) was attributed to the following factors: (i) improved surface properties of microwave heated films, i.e. less defective oxygen sub-lattice of hematite hence less surface recombination [23], (ii) the retained nanostructure and minimised grain coalescence as a result of lower processing temperatures and rapidity of the process [16]. However, the interaction of electromagnetic (EM) field with the nanostructured film is not completely understood. To begin the understanding of the microstructural changes in the microwave assisted heating process, it is vital to determine the distribution of the EM fields within the material.

The finite-difference time-domain (FDTD) technique has been widely used to model electromagnetic fields since 1980 [24,25] and its popularity has increased with the advancement of computational resources. Many papers have used electromagnetic simulations to examine the heating of food and other objects inside a microwave oven [26–29]. FDTD is also a popular simulation tool for understanding microwave assisted sintering of ceramic components [30] and has been validated using analytical solutions [31] as well as finite element methods [32]. In this paper the distribution of EM field in the specific microwave oven is modelled using FDTD. It also compares consequently calculated rate of the temperature increase with experimental measurements.

2. Methodology

In this paper the distribution of electromagnetic fields in a bespoke commercial microwave oven is modelled. The simulated results were validated against with the rate of temperature increase with experimental measurements made using a thermal imaging camera.

2.1. Experimental setup

The microwave oven used (MC8087ARS multimode cavity, LG, Milton Keynes, UK) is capable of producing a tuneable continuous power output up to a maximum of 1000 W operating at 2.45 GHz frequency. The microwave oven is fitted with thermal imaging camera (FLIR Thermovision A40, FLIR Systems, West Malling, UK) and hence the samples were centred below this: 110 mm from the door in the *Y* axis and centrally in the *X* axis. A 25 mm thick sample of porous meant the samples were raised 25 mm in the *Z* direction. Temperature was recorded using ThermaCAM Researcher software. In order to fabricate hematite electrodes using microwave heating, thin films of Fe were electrodeposited on fluorine-doped tin oxide coated (FTO, TEC8, Pilkington Glass, Ltd, St Helens, UK) glass substrates [16]. Then, microwave assisted thermal oxidation of iron films were carried out by placing the films inside a high purity alumina casket to minimise the heat loss. SiC rods were used as secondary susceptors [16]. The electric field distribution in this microwave oven is simulated in different steps so that the final configuration would match that of the experimental setup.

2.2. Simulation methodology

The FDTD method discretises the problem space into many small cuboids which define the sampling of the problem space and also the resolution of the structure – these are called Yee cells. The Yee cell splits the electric and magnetic fields into their three Cartesian components forming a discretised 3-D space lattice, see Fig. 2. Each Yee cell can have its own dielectric or metallic properties and many of these Yee cells then tessellate together to build the required structure. The Yee cells should be less than 1/10th of a wavelength to adequately sample the wave. Note, small Yee cells are required to model thin structures which increases the computational resources required. In a dielectric material, the relative permittivity, ε_r, is greater than 1, the wavelength will be reduced by a factor of $\sqrt{\varepsilon_r}$.

As FDTD works on the principle of nearest neighbour interactions, it is important for numerical stability that the wave does not propagate more than one Yee cell in each time period. This enforces a relationship between the size of the cell and the time step duration and is known as the Courant condition [24]. The electric and magnetic fields are calculated at alternate half time step intervals and are said to leapfrog each other in time. This process is continued until stability has been achieved. The electric and magnetic field values can be then found throughout this discretised space using the FDTD equations which can be easily derived from Maxwell's equations using second order accurate approximations for the finite differences [24,25]. The FDTD grid must be terminated with absorbing boundary conditions (ABC) to stop reflections from the edges of the computational domain.