



International Journal of Advanced Thermofluid Research

ISSN 2455-1368

www.ijatr.org



Development and Characterization of Novel Nanostructured $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-y}$ solid solution for Solar Electricity Generation

Ibrahim A. I. Hassan

Department of Chemistry, University of Bath, Bath, BA2 7AY, UK.

Department of Chemistry, South Valley University, 83523 Qena, Egypt.

Keywords

Solar Cells •
Water Splitting •
Hydrogen Production •
Solid Solution •
STF •
Photochemistry •
XRD.

Received

June 19, 2015

Revised

August 16, 2015

Accepted

August 25, 2015

Published

August 30, 2015

Abstract

A novel class of materials namely $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-y}$ or strontium titanate ferrate (STF) with solid solution character, suitable for solar electricity conversion, has been developed. The STF films were prepared by spray pyrolysis technique, designated as 2STF, 3STF and 4STF in the order of increasing thickness. Scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX) and Dark cyclic voltammetry (with and without illumination) studies were performed on the samples. The thicknesses of film deposits on electrodes were also measured by using a DEKTAK 6M STYLUS PROFILER system to compare with the SEM results. A blue LED was used to illuminate the samples by pulsing 'On' and 'Off' for different time intervals. The SEM images show that the homogeneity of films is directly proportional to the spraying time (thickness). The EDX measurement performed for sample 2STF has confirmed the contents Sr, Ti, and Fe. The XRD results indicate that the STF film compound may contain some material belonging to the perovskite family AMO_3 , where A and M are metals. The cyclic voltammetry measurements reveal that the developed STF is photochemically active which makes it suitable for solar water splitting application.

*Corresponding email: I.Hassan@bath.edu (Ibrahim A. I. Hassan).

DOI: <https://doi.org/10.51141/IJATR.2015.1.1.2>

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1. Introduction

Mixed metal oxides can be employed to control and improve physical properties, for example, for photo-electrochemical films. For the case of iron oxides it has been shown that strontium ferrites and strontium titanates could form solid solutions to provide control over ionic and electronic conductivity (Brixner, 1968). Mixed ionic electronic conductors (MIEC) play a core role in the manufacturing of solid-state electrochemical devices, which can be designed for energy conversion and for gas sensor applications (Rothschild and Tuller, 2006). There are many important applications for MIEC such as solid oxide fuel cell (SOFC) electrodes, oxygen separation membranes, insertion electrodes, electrochromic windows, oxygen

and gas sensors, and as catalysts (Rothschild et al., 2006). The strontium titanate ferrate (STF) family ($\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-y}$) forms a continuous solid solution between strontium titanate (SrTiO_3) and strontium ferrite (SrFeO_3) over the entire composition range $0 < x < 1$. $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-y}$ (STF) solid solution materials have been prepared (Rothschild et al., 2006) by conventional mixed-oxide techniques and by calcination of SrCO_3 , Ti, Fe mixed oxide in air at 1200 °C. The electronic structure, defect chemistry and transport properties of its members have been studied (Rothschild et al., 2006).

The related titania-doped Ruddlesden-popper ferrite ($\text{Sr}_3\text{Fe}_2\text{-xTi}_x\text{O}_{6+\delta}$) where; $0 < x < 2$, have been prepared and characterized (Brixner, 1968). This material has been prepared by conventional solid-state reaction method starting with Sr, Ti, and Fe pure oxides. After pressing the metal oxides mixture into discs under high pressure, high temperatures up to 1350 °C have been used to prepare these materials. The characterization has been reported by XRD and thermogravimetry measurements. The effect of oxygen content and titania- doping have been studied. The oxygen ion conductivity was found to decrease with increasing the titania content.

In the present work, STF-like films are prepared and investigated for photo-electrochemical applications. After failing to keep the conducting part of ITO quartz slides without damage by the effect of the very high calcination temperature 1200 °C, a low temperature approach has been investigated. STF films are prepared on ITO conducting glass by normal spray pyrolysis technique at 500 °C and via annealing in air at the same temperature for 2 hours in a furnace. Structural studies are preliminary and in-conclusive, but initial photoelectrochemical studies have revealed very promising photo-activity for water splitting.

2. Materials and Methods

2.1 Chemical Reagents

0.2 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 99.999% (Sigma-Aldrich) / MeOH, 0.1 M $\text{Sr}(\text{NO}_3)_2$ 99.995% (Aldrich) / H_2O , diisopropoxytitanium-bis-(acetylacetonate) ($\text{C}_{16}\text{H}_{28}\text{O}_6\text{Ti}$) solution, 75% wt.% (Aldrich) / isopropanol precursors have been prepared. All chemicals were obtained commercially and used without any further purification.

2.2 Instrumentation

Scanning electron microscopy (SEM) measurements were conducted by using a Jeol 6480 LV scanning electron microscope (Electron Optical Services). X-ray diffraction (XRD), and energy dispersive X-ray spectroscopy (EDX) were performed. The thicknesses of film deposits on electrodes were also measured by using a DEKTAK 6M STYLUS PROFILER system to compare with the SEM cross section data. A hotplate, a sonicator, and a furnace instrument were used for film preparation. Dark cyclic voltammetry was performed with a three-electrode system and controlled with a PGSTAT20 potentiostat (Autolab, Eco Chemie, Netherlands). For illuminated cyclic voltammetry measurements of these prepared samples an Autolab (PGSTAT 12/30) was employed for potential control and for data recording. A blue LED (Farnell, wavelength 455 nm) was used to illuminate samples. The illumination was carried out by pulsing 'On' and 'Off' for different time intervals (typically 0.4 s 'On' and 0.2 s 'Off').

2.3 Experimental Setup of Measurement Cells

All the measurements have been performed in a specially designed three electrode cells, called photoelectrochemical cell (Figure 1). The photoelectrochemical cell is made from 'PTFE glass filled' material (designed at the University of Bath). The cell consists of two main parts connected together by means of four screws; the body and the lid as shown in Figure 2 and Figure 3.

The body of the cell (Figure 4) consists of two separated compartments. The bigger compartment is for the electrolyte in which both the reference electrode (Ag/AgCl) and the counter electrode (Pt) were immersed. The body has a hole in the middle which allows light to go through. Quartz windows were used in order to contain the solution in the cell and be transparent to the light. The lid was designed to hold the reference and counter electrode and also has small holes to let gases out during the reactions. The working electrode was held in the smaller compartment of the cell. A screw was used to fix the working electrode to be in touch with the electrolyte through a specific area of 0.5 cm diameter circular open window between the two compartments of the cell, with an active area of the working electrode of 0.38 cm^2 . The light was incident through a quartz window with the same diameter 0.7 cm. There is a window in both of the cell sides for SE and EE illumination. A special designed cell holder has been made from stainless steel (Figure 5) to fix the cell in a Faraday box.

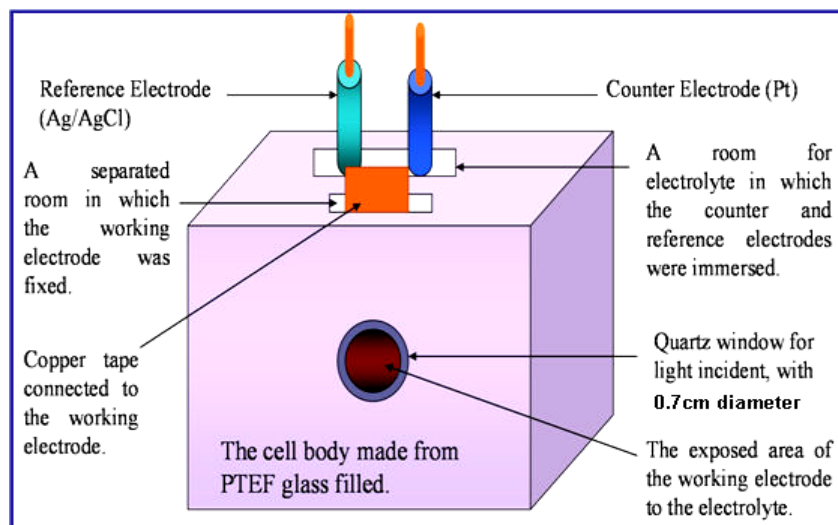


Figure 1. Schematic of the specially designed photoelectrochemical cell.

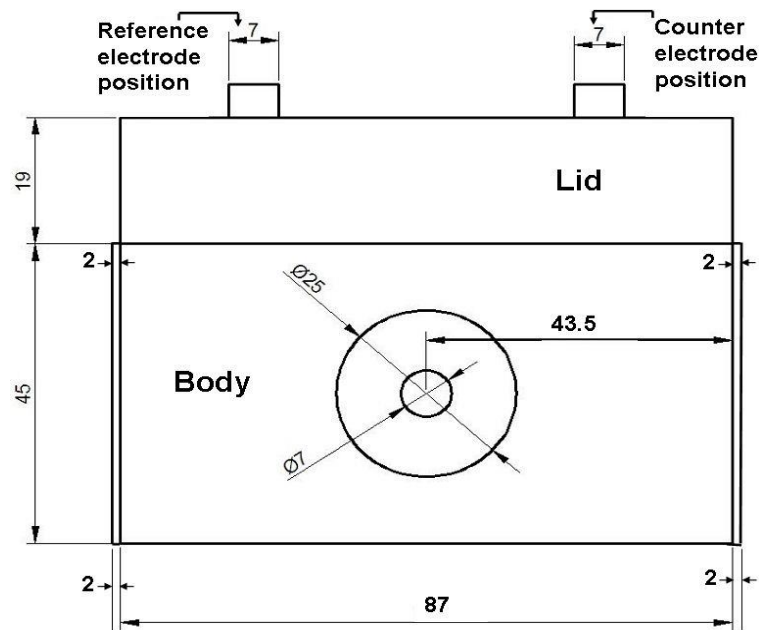


Figure 2. Back side and lid of the photoelectrochemical cell.

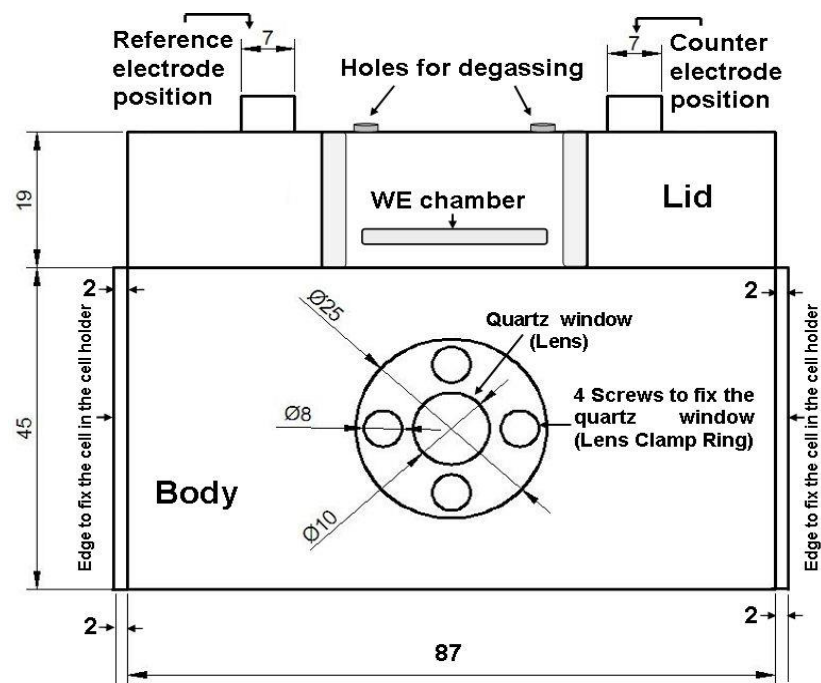


Figure 3. Front side and lid of the photoelectrochemical cell.

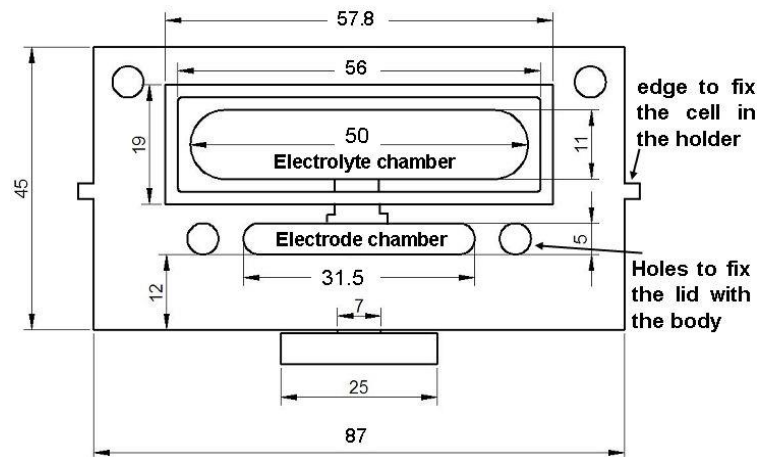


Figure 4. Top view of the photoelectrochemical cell.

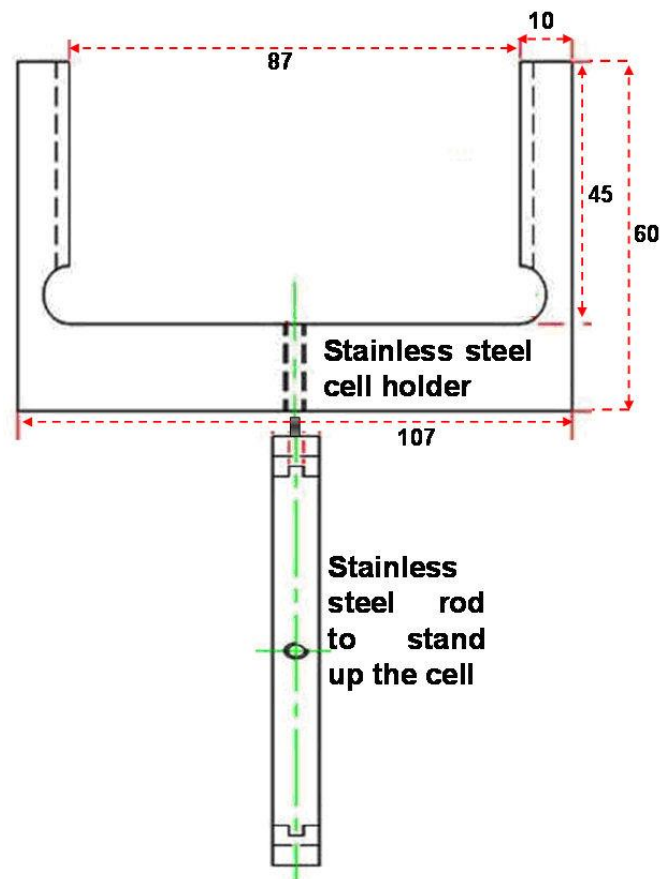


Figure 5. Stainless steel holder for the photo-electrochemical cell.

Most experiments were conducted in aqueous 1 M NaOH solution electrolyte. Only for the experiments with WO_3 film electrodes 1 M H_2SO_4 has been used. Electrolyte solutions were prepared using filtered and demineralised water. Phosphate buffer solution pH 11 was used as an electrolyte in some Fe_2O_3 film

electrode experiments. De-aeration of the electrolyte was achieved by bubbling argon gas for 5 minutes prior to each experiment.

2.4 Procedure for Spray Pyrolysis

The indium-doped tin oxide (ITO) slide was cleaned by sonication at 40 °C for 15 minutes in, sequentially, detergent (5 vol% decon-90), isopropanol, acetone and finally in ethanol, in which the slides were kept. A mixture of the above precursors, with the concentrations as shown in the chemical reagents, has been prepared to contain 50 wt.% Fe, 25 wt.% Sr, and 25 wt.% Ti. So it was taken 93.36 mL of 0.1 M Sr(NO₃)₂/H₂O, 31.77 mL of 0.2 M Fe(NO₃)₃·9H₂O/MeOH and 8.33 mL of diisopropoxytitanium-bis-(acetylacetonate) (C₁₆H₂₈O₆Ti) solution and they are mixed together. Stirring of the mixed precursor has been carried out for 10 minutes, on an electric stirrer, to ensure of completely mixing the precursors as a dark violet solution. The ITO slide has been dried with nitrogen gas and then preheated to ~ 500 °C on a hotplate and then 50 mL of the mixed precursor (at room temperature ~22 °C) has been sprayed by using a manual spray bottle (Figure 6) and by spraying two sprays on three different spots along the slide every 10 seconds. Different spraying times have been used to obtain different thicknesses. The slide left on the hotplate for 10 minutes and then annealed in the furnace at 500 °C for further 2 hours.



Figure 6. The manual spray bottle connected to a squeezable rubber pump, used in Spray Pyrolysis method.

3. Results and Discussion

3.1 Morphology and Structural Studies

Samples of strontium titanate ferrate (STF) have been prepared by the spray pyrolysis method on ITO conducting glass slides at 500 °C followed by 2 hour annealing in air at 500 °C. Table 1 shows types of samples produced at different spraying times. The average thickness has been estimated based on profilometry and SEM measurements. The SEM images show that the films are not completely homogenous

when studied over a wider area (samples 2STF and 3STF, Figure 6 a, and b) while being more homogenous with grains of ca. 20 nm to 200 nm (sample 4STF, Figure 6c).

Table 1. STF samples prepared by spray pyrolysis method at 500°C for different spraying times

Sample	Substrate	Spraying time (min)	Approx. average thickness
2STF	ITO	4	1.1 (+/-0.2) μm
3STF	ITO	3	1.0 (+/-0.2) μm
4STF	ITO	5	1.2 (+/-0.2) μm

Additional EDX measurement have been performed for sample 2STF (Figure 6d) and it shows that the sample contains Sr, Ti, and Fe. The accuracy of EDX in this case is not sufficient to confirm the elemental composition, but based on the ratio of starting materials a composition Sr:Ti:Fe of 1:1:2 is expected. Figure 7 shows the cross section of sample 2STF and that of 4STF which indicates that the thickness of these films is about 1.1 μm in average, but an error of at least +/- 0.2 μm has to be assumed. The films are visible by eye as a dark reddish-brown colour.

3.2 X-Ray Diffraction

XRD results showed that the main peak in STF films could be explained as due to the orientation (112) which is the main peak in the related structure of Sr(Fe_{0.9}Ti_{0.1})O_{2.95} according to published literature data by Adler et al. (2000). This result indicates that the STF film compound may contain some material belonging to the perovskite family AMO₃, where A and M are metals. The peaks of the ITO substrate are described with (*) symbols (Figure 8). According to the preparation procedures it was expected that the overall chemical composition is given by (SrFe)(TiFe)O₆ which could result in the formation of a perovskite-type(a) structure. However, evidence for this structure is currently weak and in future additional experiments confirming the type of structure and structural homogeneity are required. (a)A perovskite (Wenk et al., 2004) is the material with the crystal structure like calcium titanium oxide (CaTiO₃), or A₂B₄X₂-3.

In order to obtain a better estimate for the average crystallite size in STF films, the Scherrer method (,) has been used (Scherrer equation 1)

$$B_{FWHM}(2\theta) = \frac{K\lambda}{L \cos\theta} \quad (1)$$

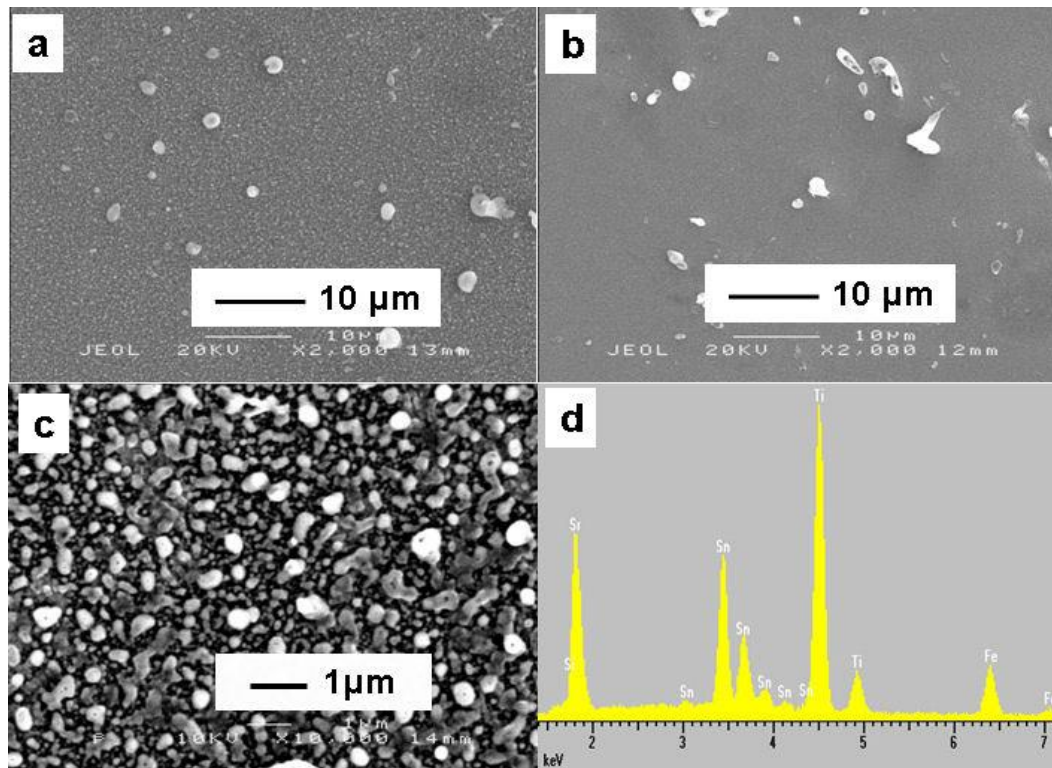


Figure 6. Typical SEM images of samples a: 2STF, b: 3STF, and c: 4STF. d: EDX of sample 2STF showing the presence of Sr, Ti, and Fe.

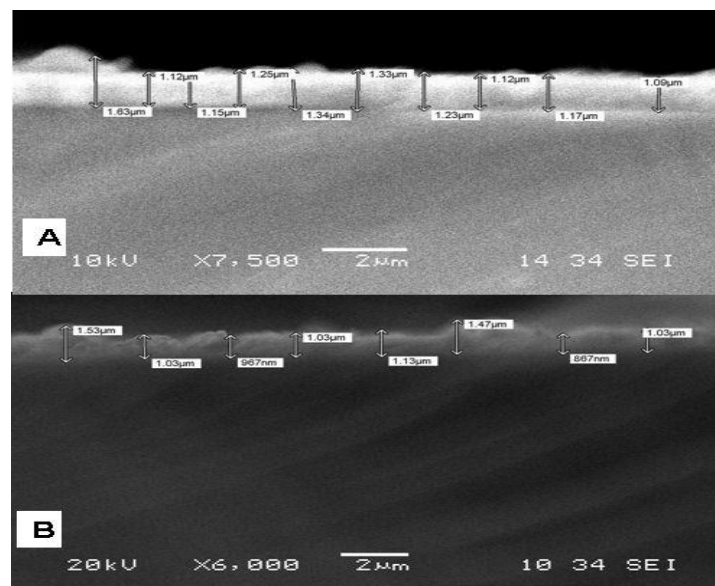


Figure 7. SEM cross section images of A: 2STF, and B: 4STF.

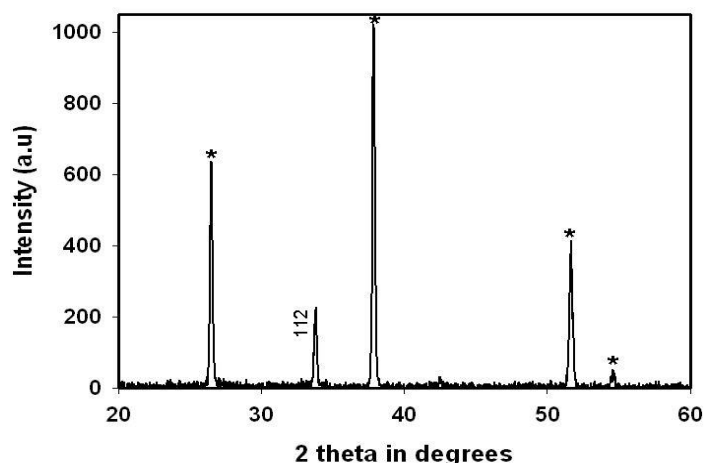


Figure 8. XRD for sample 2STF (* denotes ITO diffraction peaks).

According to the conventional Full Width at Half Maximum method (FWHM), the Scherrer constant is assumed here approximately $K = 0.94$. The wavelength of X-ray radiation is $\lambda(\text{Cu-K}) = 1.5406 \text{ \AA}$. With a typical width at half height of $\text{BFWHH} = 0.15$ degrees (for the (112) peak in Figure 8). The estimated grain or crystal size is approximately 1 nm, which is very small. This estimate could be affected by instrumental parameters and should be seen as a very rough estimate, but it shows that the low calcination temperature may have resulted in very small grains. The fact that only one dominant peak is observed is promising, and this is in agreement with a reasonably homogeneous material.

3.3 Dark and Illuminated Cyclic Voltammetry

Cyclic voltammograms have been measured first without illumination for samples immersed in aqueous 1 M NaOH. From the voltammograms (Figure 9) it was found that there are strong reduction peaks at applied potential -0.9 V. In contrast, the oxidation peaks are relatively small and observed at an applied positive potential of 0.7 V. The additional reduction is likely to be associated with the Ti(IV/III) rather than the Fe(III/II) process. The oxidation or reduction peaks were found to be relatively independent of the film thickness.

Next voltammetric measurements were performed with illumination. Flashing blue LED ($\lambda = 455 \text{ nm}$) light was used in illuminating the STF samples to measure the characteristic photocurrents. Light has been controlled through a LED driver and PPR1 wave generator and gives pulses as 0.4 seconds 'On' and 0.2 seconds 'Off'. Figure 10 shows the typical photocurrent response obtained by illumination of the SE side of sample 3STF. It was found that the photocurrent reaches about 1 mA/cm^2 at applied potential 650 mV under illumination by blue LED at 10.9 mW cm^{-2} . Similar results were obtained with samples 2STF and 4STF.

This indicates that these materials are promising photochemically active and they can be used for example in the tandem cell for water splitting purposes. It was also found that for these materials the SE photocurrent is higher than that of EE one, which can be due to the relatively high porosity of these film materials with sufficient electrolyte contacting the substrate electrode. The SE photocurrent increases with increasing the spraying time with sample 2STF giving slightly higher currents. It can be noticed from the

transient peaks (Figure 10) that there are still high recombination rates destroying the generated hole-electrons pairs. Sharp peak transients can be seen especially at lower applied potentials. This high recombination might due to the presence of the trapping sites between the particles of different oxides components.

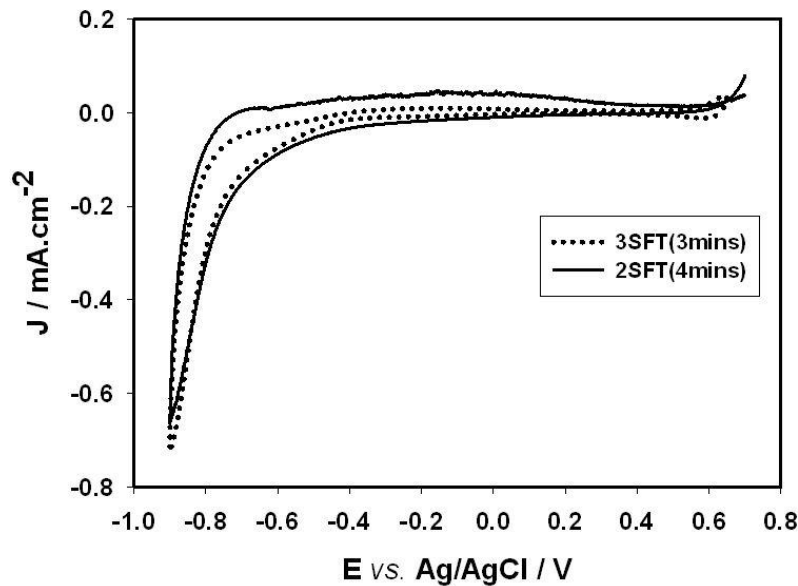


Figure 9. Comparison between dark cyclic voltammograms for samples 3STF (sprayed for 3 minutes) and 2STF (sprayed for 4 minutes) immersed in 1 M NaOH recorded with a scan rate 0.1Vs^{-1} vs. Ag/AgCl

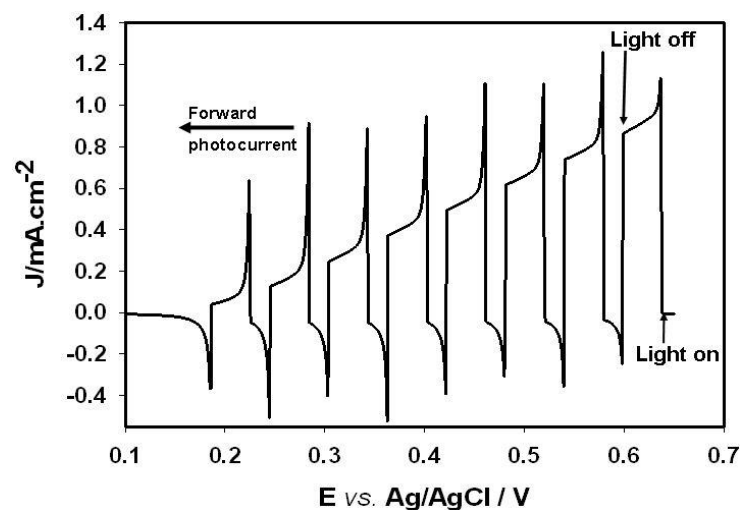


Figure 10. Pulse-illuminated voltammogram for sample 3STF (sprayed for 3 minutes) SE immersed in 1 M NaOH at a scan rate 0.1Vs^{-1} , using a blue LED with $10.9\text{mW}/\text{cm}^2$.

4. Conclusions

The spray pyrolysis method has been successfully applied to prepare novel low temperature strontium titanate ferrate (STF) solid solution suitable for solar water splitting. According to XRD results it was found that the film material is consistent with Sr(Fe_{0.9}Ti_{0.1})O_{2.95}, which indicates that this compound may be from the perovskite family AMO₃. The material has been prepared in a nano-scale form on ITO conducting glass substrates. The homogeneity of films is found to be directly proportional to the spraying time (thickness). The EDX measurement has confirmed the contents Sr, Ti, and Fe. The cyclic voltammetry measurements reveal that the developed STF is photochemically active which makes it a suitable candidate for solar water splitting application. A lot more work will be necessary to develop these types of material in the future.

Acknowledgements

The author would like to thank Professor Laurie M. Peter and Professor Frank Marken, Department of Chemistry, University of Bath, Bath, UK for their kind help during this work. Many thanks to Dr. Gabriele Kociok-Köhn in the Department of Chemistry, University of Bath, Bath, UK for XRD measurements. Thanks are also due to Mr. Hugh Perrott and Dr. John M. Mitchels in the Department of Physics, University of Bath, Bath, UK for SEM and EDX measurements. Finally, the author expresses deepest thanks to the Egyptian Government for funding.

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