# Investigation of $PO_4^{3-}$ oxyanion-doping on the properties of $CaFe_{0.4}Ti_{0.6}O_{3-\delta}$ for potential application as symmetrical electrodes for SOFCs.

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## Abstract

In this work, the incorporation of $PO_4^{3-}$ into $CaTi_{0.6-x}Fe_{0.4}P_xO_{3-\delta}$ ($0 \leq x \leq 0.75$) perovskite series is amply studied. Samples are analysed by using the Rietveld method and pure phase compounds with a cubic perovskite structure (s.g. $Pm\bar{3}m$) are obtained for $x \leq 0.025$; $Ca_{10}(PO_4)_6(OH)_2$ is identified as secondary phase when the doping level is further increased. The redox stability is enhanced after P-doping. A complete electrochemical characterization is reported, including conductivity measurements in both oxidizing and reducing atmospheres. Conductivity values of the P-doped samples are slightly higher than that of the undoped one, i.e. 0.11 and 0.07 $Scm^{-1}$ for $CaTi_{0.575}Fe_{0.4}P_{0.025}O_{3-\delta}$ and $CaTi_{0.6}Fe_{0.4}O_{3-\delta}$, respectively, at 750 ºC in air. The performance of $CaTi_{0.575}Fe_{0.4}P_{0.025}O_{3-\delta}$ acting simultaneously as both anode and cathode was also tested in a symmetrical solid oxide fuel cell with a 240 μm thick YSZ electrolyte. Hence, these results show that $PO_4^{3-}$ units can be introduced into $CaTi_{0.6}Fe_{0.4}O_{3-\delta}$ perovskite structure, having beneficial effects on the electrochemical performance and the phase stability.

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## 1. Introduction

A typical Solid Oxide Fuel Cell (SOFC) is comprised of three specific ceramic elements: cathode, electrolyte and anode, all of them with well-defined compositions. This heterogeneity leads to numerous fabrication steps during the assembly of the device, with the concomitant losses of energy, money and time, as well as the possibility of not desired reactivity between the cell components during these stages.

All these disadvantages could be solved with a new SOFC configuration, symmetrical solid oxide fuel cells (SSOFCs), where cathode and anode are the same material with good stability and adequate electrochemical properties in both oxidising and reducing conditions [1-5]. This approach largely simplifies the manufacturing process, since both electrodes are deposited and sintered in only one thermal treatment. This also results in lower fabrication costs and improved chemical and mechanical stability of the device since the same type of interface is presented on both sides of such cell.

Diverse families of materials have been tested as promising electrodes for SSOFCs, such as $Pr_2NiO_{4\pm\delta}$, $Nd_2MnO_{4\pm\delta}$ and $La_{0.5}Sr_{1.5}MnO_{4\pm\delta}$ systems with the Ruddlesden-Popper structure; $La_2CoTi_{0.7}Mg_{0.3}O_{6-\delta}$ and $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ double perovskites; and $PrNi_{0.4}Fe_{0.6}O_{3-\delta}$, $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$, $La(Fe,Ni)O_{3-\delta}$, $SrFeO_{3-\delta}$ and $SrCoO_{3-\delta}$ simple perovskites, which is the system more extensively studied for these type of applications [5-17].

$ATiO_3$ (A=Ca, Sr, Ba) perovskites with partial replacement of titanium by iron have been hugely studied due to the significant interest of creating mixed ionic and electronic conductivity when these perovskites are doped with different multivalent cations [18]. The structure of iron-substituted calcium titanates was firstly characterized by Grenier *et al.* using X-ray diffraction, transmission electron microscopy and Mössbauer spectroscopy studies [19,20]. The $CaTi_{1-y}Fe_yO_{3-\delta}$ system is described as an intermediate material between two structures, the $CaTiO_3$ perovskite and the $Ca_2Fe_2O_5$ brownmillerite. The importance of such compounds lies in their ability to accommodate anion vacancies and therefore support the electrical neutrality when $Ti^{4+}$ is interchanged by $Fe^{3+}$ [18,21-29]. The electronic and ionic conductivity of $CaTi_{1-y}Fe_yO_{3-\delta}$ depend on the oxygen vacancy concentration and the degree of ordering of the oxygen sublattice, which determines their mobility. Oxygen vacancies are randomly allocated for samples with $y<0.5$, however, long-range ordering occurs when $y\geq0.5$ [30]. Such ordening of the oxygen vacancies is detrimental for practical implementations, since it seriously reduces the ion conduction and also decreases the concentration and mobility of hole carriers [30]. In this context, $CaTi_{0.6}Fe_{0.4}O_{3-\delta}$ is the composition with the highest Fe-content and disordered oxygen vacancies.

Recently, simple perovskites ($ABO_3$) have been modified by the incorporation of oxyanions, such as $BO_4^{5-}$, $SiO_4^{4-}$ and $PO_4^{3-}$, into the ionic framework [31-34]. Under this approach, the octahedral $BO_6$ unit is replaced by a tetrahedral oxyanion, and therefore, generating two oxide vacancies that favours the ionic conductivity. Moreover, in order to maintain the lattice electroneutrality, the $B^{n+}$ species are reduced to $B^{(n-1)+}$, creating an effect of electron doping, which enhances the electronic conductivity. Hence, oxyanion doping is a promising strategy to improve the properties of the materials for the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR). This approach has been successfully applied to different systems, such as $CaMnO_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $SrFeO_{3-\delta}$, where oxyanion doping leads to an enhancement of the electrical properties as well as the stabilization of high symmetric phases [35-37]. Recent works have extended the applications of such phosphate doped perovskites to low temperature oxygen evolution reaction (OER) and ORR catalysts [38-40].

The aim of this work is to explore the effect of the incorporation of $PO_4^{3-}$ units into the framework of $CaTi_{0.6}Fe_{0.4}O_{3-\delta}$ perovskite and examine its influence on the structural, electrical and redox stability properties, with the goal of its potential application as electrodes for SSOFCs.

## 2. Experimental

### 2.1. Synthesis

Materials with composition $CaTi_{0.6-x}Fe_{0.4}P_xO_{3-\delta}$ (x = 0, 0.025, 0.05 and 0.075) were prepared by using the freeze-drying method and the same synthetic procedure detailed in previous works for comparable materials [41]. Stoichiometric solutions of $CaCO_3$ (99%, Alfa Aesar), $Ti[OCH(CH_3)_2]_4$ (99%, Aldrich), $Fe(NO_3)_3{\cdot}9H_2O$ (99.95%, Aldrich) and $(NH_4)_2HPO_4$ (99%, Aldrich) were elaborated by dissolving in different beakers $CaCO_3$ in diluted nitric acid, $Ti[OCH(CH_3)_2]_4$ in absolute ethanol, and $Fe(NO_3)_3{\cdot}9H_2O$ and $(NH_4)_2HPO_4$ in distilled water. An ethylenediaminetetraacetic acid solution (99.99%, Aldrich) was incorporated as a complexing agent into the different metallic salts in a molar ratio 1:1. After that, all cation solutions were combined, getting a transparent solution with concentration of 0.1 mol $L^{-1}$ and pH~8. Precursor solutions were slowly dripped and frozen into liquid $N_2$ and then dehydrated in a Scanvac Coolsafe freeze-dryer for 48 hours, obtaining dried powders which were calcined at 300 and 800 ºC for 1 h to remove the organic material and the remaining carbonaceus species, respectively.

The resulting powders were compacted into cylindrical disks of 10 and 1 mm of diameter and thickness, respectively, and sintered at 1200 and 1400 ºC for P-doped and undoped samples,

respectively, for 4 h with heating/cooling rates of 5 ºC $min^{-1}$. Hereafter, $CaTi_{0.6-x}Fe_{0.4}P_xO_{3-\delta}$ samples are labelled as $P_x$ where x is the phosphorus content.

### 2.2. Structural, microstructural and thermal characterisation

Laboratory X-ray powder diffraction (XRPD) was employed to analyse the composition and structure of all the compounds. The diffractometer used was a PANalytical X´Pert Pro MPD equipped with a X´Celerator detector and $CuK_{\alpha 1}$ radiation. The phase identification and structural analysis were performed using the X'Pert HighScore Plus and GSAS softwares [42,43].

The morphology and composition of the pellets were examined by field emission scanning electron microscopy (FEI-SEM, Helios Nanolab 650) and energy-dispersive X-ray spectroscopy (EDX, Oxford Instruments). The grain size was estimated by the linear intercept method [44].

The phase stability in reducing atmosphere was investigated by exposing the powder to a regular 5%$H_2$-Ar flow at 800 ºC for 2 days. For the chemical compatibility studies, the $CaTi_{0.575}Fe_{0.4}P_{0.025}O_{3-\delta}$ sample and commercial electrolyte powder, $Zr_{0.84}Y_{0.16}O_{1.92}$ (YSZ, Tosoh), were mixed in a 50 wt.% and annealed in air at different temperatures for 1 day. The resulting mixtures were analysed by XRPD.

The Oxygen stoichiometry was calculated by thermogravimetric analysis (Mettler Toledo) from 30 to 1200 ºC under a 50 mL $min^{-1}$ $N_2$ flow and a heating/cooling rate of 10 ºC $min^{-1}$.

### 2.3. Electrical characterisation

Impedance spectra were obtained by using a Solartron 1260 FRA in two different atmospheres: air (for cathode applications) and 5%$H_2$-Ar (for anode applications). The data were acquired in intervals of 50 ºC from 800 down to 150 °C with an ac perturbation and a stabilization time between successive measurements of 100 mV and 45 min, respectively. Pt-ink (METALOR® 6082) was deposited on the both sides of the pellet surfaces, and a heating treatment at 800 ºC for 15 min was carried out to sinter the Pt current collectors.

### 2.4. Fuel cell performance

Electrolyte supported cells were prepared to investigate the electrochemical performance of the P-doped samples in SOFC conditions. The electrolyte was prepared by compacting commercial YSZ powders (Tosoh) into a disk of 13 and 0.25 mm in diameter and thickness, respectively, following by sintering at 1400 ºC for 4 h. An ink was prepared from the P-doped powders and Decoflux™ (Zschimmer & Schwarz) and was symmetrically screen-printed on both faces of the YSZ pellet, which was finally sintered at 1000 ºC for 1 h. The area where the symmetrical electrodes were deposited was restricted to 0.25 $cm^2$. A ceramic paste (Ceramabond 668, Aremco) was employed to

seal the symmetrical cell on an alumina device. The impedance and current-voltage plots were acquired using a Bio-Logic VSP potentiostat/galvanostat/FRA in the 650-800 ºC temperature range. Static air and $H_2$ were employed as oxidant and fuel, respectively.

## 3. Results and discussion

### 3.1. Single phase existence range

The undoped sample is a single phase with cubic type structure after sintering at 1400 ºC, in accordance with Becerro *et al.* [45]. At lower temperatures impurities of $Ca_2Fe_2O_{5+\delta}$ are detected (Figure 1a). In contrast, the introduction of a small amount of $PO_4^{3-}$ units into the perovskite structure leads to a reduction of the synthesis-sintering temperature to 1200 ºC (Figure 1b).

XRPD patterns for the $CaTi_{0.6-x}Fe_{0.4}P_xO_{3-\delta}$ series (x = 0, 0.025, 0.05 and 0.075) are shown in Figure 2. The compounds with P content $x \leq 0.025$ are single phase materials, higher dopant content leads to an increasing segregation of $Ca_{10}(PO_4)_6(OH)_2$ with an apatite-type structure (PDF number 96-901-3628) as a secondary phase (Table 1); however, despite this segregation, the whole series crystallize with a cubic perovskite-type structure.

XRPD data were analysed by using the Rietveld method and a cubic perovskite-type structural model, with a $Pm\bar{3}m$ space group, was employed for all the refinements. Occupancy factors were fixed to the nominal stoichiometry, where Ti, Fe and P were located in the same crystallographic position, and their isotropic atomic displacement parameters constrained to be the same. Parameters such as unit cell, scale factor, background, peak shape and isotropic displacement were refined. All samples were satisfactorily refined, obtaining favourable agreement factors (Table 1). An example of these fits is shown for $P_{0.025}$ in Figure 3. It has to be mentioned that the agreement factors were slightly worse for the undoped composition, $P_0$, in comparison with the P-doped samples, likely due to a small orthorhombic distortion that disappeared after doping due to the stabilizing effect of phosphorus.

The evolution of the unit cell volumes with the P content is shown in Table 1. In these series, a decrease of the unit cell volume is detected as the P content increases up to x=0.075. It is important to bear in mind for oxyanion-doped samples that the evolution of the cell parameters is a balance between two factors: (i) the smaller size of the tetrahedral $PO_4$ units in comparison to that of the octahedral $TiO_6$, which would lead to a decrease of the cell volume; and (ii) the replacement of the $TiO_6$ unit by the $PO_4$ one leads to the loss of two oxygens and the concomitant reduction of $Fe^{4+}$ (0.585 Å) to $Fe^{3+}$ (0.645 Å) in order to maintain the lattice electroneutrality, which results in an increase of the cell volume, according to the following equation:

$(NH_4)_2HPO_4 + 4Fe_{Fe}^{X} + O_O^X \rightarrow P_{Fe}^{\cdot} + 3Fe_{Fe}' + V_O^{\cdot\cdot} + 2NH_3 + 3/2H_2O + 3/4O_2 + \text{“}FeO_2\text{”}$ **Eq.1**

It has to be mentioned that “$FeO_2$” does not mean free iron oxide but $Fe^{4+}$ that maintains its oxidation state after the oxyanion doping [37].

As can be seen in Table 1, for the whole $CaTi_{0.6-x}Fe_{0.4}P_xO_{3-\delta}$ series, the small size of phosphorus tetrahedral outweighs the iron reduction, for $0 \leq x \leq 0.075$, indicating that despite the segregation of $Ca_{10}(PO_4)_6(OH)_2$, part of the phosphorus is being still incorporated into the structure, leading to a decrease of the cell volume.

All samples were also analyzed by thermogravimetric analysis to determine the oxygen stoichiometry, following a comparable process described in the literature [36,37]. The mass losses of the samples are utilized to calculate the average oxidation state of the iron cations and the oxygen stoichiometry. As can be appreciated in Figure S1, both the oxygen deficiency (δ) and the average oxidation state of iron cations decrease with the P-content, i.e. oxidation states of 3.110 and 3.042 for $P_0$ and $P_{0.075}$, respectively. These results confirm that most of the iron is present as $Fe^{3+}$, as expected, although a small contribution of $Fe^{4+}$ is possibly presented, in accordance with previous Mössbauer spectroscopy studies for related compounds [46]. The amount of $Fe^{3+}$ increases with the P content because the introduction of $PO_4^{3-}$ leads to the reduction of $Fe^{4+}$ to $Fe^{3+}$ to maintain the lattice electroneutrality (Eq. 1).

### 3.2. Phase stability under reducing conditions

Structural stability in reducing conditions is a key factor in order to use these materials as symmetrical electrodes in SSOFCs. Partial decomposition or structural changes of the electrode phases might produce volume alterations during the reduction and oxidation cycles, causing delamination in the cell. Thus, in order to ensure the reliability of these P-doped compounds under reducing conditions, stability tests were conducted.

In Figure 4 it can be seen that the undoped composition, $P_0$, is unstable under such reducing conditions, leading to a variation in symmetry, from a cubic to an orthorhombic phase. This modification is due to the partial reduction of Fe to lower oxidation states, which causes oxygen losses in the structure and modification of the oxygen sublattice. An opposite behaviour is observed for the P-doped samples, which are stable under the same reducing conditions and maintain the cubic symmetry, including those with $Ca_{10}(PO_4)_6(OH)_2$ as secondary phase. In addition, the cell parameters for the whole series increase after the thermal treatment in reducing conditions, due to the change from $Fe^{4+}$ to $Fe^{3+}$ (Table 1). Therefore, these results highlight the beneficial effect of the incorporation of phosphorus into the structure, leading to an enhancement in the redox stability and its possible use as symmetrical electrode for SOFCs.

### 3.3. Microstructural characterisation

Figure 5 shows the superficial SEM images of the $P_{0.025}$, $P_{0.05}$ and $P_{0.075}$ samples sintered at 1200 ºC for 4 h. These images reveal that the ceramic pellets are well sintered with densities higher than 96%. Analysis of the P-doped samples indicates that the incorporation of phosphorus into the structure does not change significantly the microstructure of the materials, with an average grain size of 2 μm (Figure 5a-c). However, $P_{0.075}$ exhibits slightly smaller grain ~1 μm, possibly due to the presence of larger amounts of secondary phases.

EDX mapping for $P_{0.025}$ reveals that there is a good bulk distribution for all the elements and phase segregations at the grain boundaries are not detected (Figure 5d). However, for $x \geq 0.05$, P-enriched grains are observed, ascribed to the $Ca_{10}(PO_4)_6(OH)_2$ segregation, which increases with the P-content (Figure 5e and f). These results confirm the extremely low solubility of phosphorus in the $CaTi_{0.6}Fe_{0.4}O_{3-\delta}$ structure, which is in agreement with the XRPD data.

### 3.4. Chemical compatibility

The reactivity between the different components of the cell is an important aspect to be considered during the fabrication of a SSOFC, the formation of interfacial phases between the materials might increase the ohmic resistance and partially block the oxide ion transport. Furthermore, a poor adherence of the electrodes might lead to a high contact resistance and even delamination of the layers. Thus, it is vital to know the optimal fixing temperature to minimize the formation of such reaction products at the interface between the electrolyte and the electrodes layers.

Taking into consideration that the minimum temperature required to obtain an optimal adherence of these P-doped materials with YSZ electrolyte is 1000 ºC, the chemical compatibility study was carried out up to this temperature. Figure S2 shows the XRPD patterns of the mixtures of $P_{0.025}$ electrode with YSZ electrolyte at different temperatures for 24 h. Neither appreciable undesired phases nor variation in the cell parameters were observed, indicating that these compounds are chemically compatible to be used simultaneously in a cell in the temperature range studied between 800 and 1000 °C.

### 3.5. Electrical characterisation

According to the literature data, the he conductivity of $CaTi_{1-y}Fe_yO_{3-\delta}$ series is very sensitive to the temperature and the oxygen stoichiometry [28]. Moreover, the oxyanion doping has a large influence on the electronic and ionic conductivity of similar perovskite structure materials [3,36]. The conductivity of these series was measured in two different atmospheres: air and 5%$H_2$-Ar. For all samples, the conductivity variation with the temperature shows a semiconductor-type behaviour in the whole temperature range investigated. In oxidising conditions, the conductivity of the $CaTi_{0.6-}$

$_xFe_{0.4}P_xO_{3-\delta}$ series increases up to x = 0.05, associated with the incorporation of phosphorus into the structure, which increases the oxygen vacancy concentration as demonstrated earlier by the defect equation (Eq. 1). Higher P-content leads to a decrease in conductivity possibly due the disrupting effect of phosphorus segregations.

In order to prove the beneficial effect of P-doping, and its incorporation into the structure, a phosphorus-free sample derived from $CaTi_{0.575}Fe_{0.4}P_{0.025}O_{3-\delta}$ was prepared, with formula $CaTi_{0.575}Fe_{0.4}O_{3-\delta}$ and cation deficient in the perovskite in B-site. As can be seen in Figure 6a, the conductivity of this sample decreases significantly with values even lower than those of the undoped composition. These results clearly confirm that the improvement of conductivity in P-doped samples is due to the replacement of octahedral $TiO_6$ units by tetrahedral $PO_4$ ones.

In reducing conditions the conductivity decreases for all compositions due to the almost complete reduction of $Fe^{4+}$ to $Fe^{3+}$, resulting in a significant decrease of the charge carriers, which is mainly associated with electron-hopping (Figure 6b). However, the conductivity of the $P_{0.025}$ sample in reducing conditions is slightly higher than the undoped one, i.e. 0.11 and 0.07 $Scm^{-1}$, respectively, at 750 ºC, likely due to higher number of oxygen vacancies (Eq. 1) and the improved stability of the cubic phase on P-doping, whereas $P_0$ decomposes in reducing conditions.

### 3.6. Fuel cell test

Fuel cell tests were carried out to prove that P-doped samples can operate simultaneously as both anode and cathode in SSOFC. Figure 7a shows the power density and the current-voltage curves for $P_{0.025}$/YSZ/$P_{0.025}$ electrolyte-supported cell at different temperatures. The open circuit voltage (OCV) matches well with the theoretical value expressed by the Nernst equation (~1.1 V). This cell generated a maximum power density of 58 $mWcm^{-2}$ at 800 ºC. This value is not extremely high due to the high ohmic resistance of the thick YSZ electrolyte. $P_0$/YSZ/$P_0$ electrolyte-supported cell was not prepared since the undoped composition, $P_0$, is not stable under reducing conditions as previously discussed. Figure 7b shows a cross-sectional image of this cell. The adhesion between the electrolyte and the symmetrical electrodes is quite good and an adequate porosity is observed after the electrical characterization, without appreciable delamination or reactivity at the electrode/electrolyte interface. The electrolyte is fully dense and has a thickness around 240 μm. Thus, the power density values could be considerably improved by decreasing the electrolyte thickness.

In summary, the results obtained in the present work suggest that P-doped $CaTi_{0.6}Fe_{0.4}O_{3-\delta}$ samples are alternative and promising symmetrical electrode materials for SOFCs. However, further investigation is necessary to improve the performance by optimizing the microstructure of the cell,

i.e. by reducing the thickness of the electrolyte or alternatively by using nanostructured electrodes obtained by low deposition methods, such as spray-pyrolysis [47,48].

## Conclusions

$CaTi_{0.6-x}Fe_{0.4}P_xO_{3-\delta}$ series (x = 0, 0.025, 0.05 and 0.075) have been prepared by the freeze-dried precursors method, obtaining single phase compounds for $x \leq 0.025$. The introduction of a small quantity of $PO_4^{3-}$ units into the $CaTi_{0.6-x}Fe_{0.4}P_xO_{3-\delta}$ structure reduces the synthesis-sintering temperature from 1400 to 1200 ºC. The unit cell volumes decrease with increasing P-content without a significantly change in the morphology of the materials. Phosphorus enriched zones, ascribed to $Ca_{10}(PO_4)_6(OH)_2$ segregations, were detected by EDX analysis for $x \geq 0.05$, confirming the extremely low solubility of the phosphate groups in the structure. Annealing experiments in 5%$H_2$-Ar showed improved redox stability for the P-doped compounds in contrast to the undoped one. Moreover, the conductivity values for P-doped samples are slightly higher than those of the undoped one in both oxidising and reducing atmospheres. Hence, these results show that phosphorus can be successfully incorporated into calcium iron titanate perovskites, having beneficial effects on the conductivity and phase stability in both oxidising and reducing conditions, making these compounds potentially suitable for symmetrical electrode applications. This work also shows the first results for the performance of a SOFC with symmetrical oxyanion-doped electrodes and suggest that further studies on related materials with optimized electrode microstructure are warranted. Furthermore, they may have other potential applications, given recent reports of phosphate doped perovskites as low temperature OER/ORR catalysts.

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**Table 1.** Cell parameters and normalized cell volumes for $CaTi_{0.6-x}Fe_{0.4}P_xO_{3-\delta}$ series (x = 0-0.075) in air and 5%$H_2$-Ar obtained from XRPD data analysis.

| | | $P_0$ | $P_{0.025}$ | $P_{0.05}$ | $P_{0.075}$ |
|---|---|---|---|---|---|
| **Air** | **a (Å)** | 3.8321(1) | 3.8287(1) | 3.8277(1) | 3.8271(1) |
| | **V/Z(Å$^3$)** | 56.27(1) | 56.13(1) | 56.08(1) | 56.05(1) |
| | **$R_{WP}$(%)** | 3.82 | 2.45 | 2.60 | 2.67 |
| | **$R_F$(%)** | 4.79 | 4.42 | 4.45 | 4.76 |
| | **$Ca_{10}(PO_4)_6(OH)_2$(%)** | - | - | 2.4 | 4.0 |
| **5%$H_2$-Ar** | **a (Å)** | 5.4225(3) | 3.8359(1) | 3.8362(1) | 3.8364(1) |
| | **b (Å)** | 5.4576(3) | - | - | - |
| | **c (Å)** | 7.6702(3) | - | - | - |
| | **V/Z(Å$^3$)** | 56.75(3) | 56.44(1) | 56.45(1) | 56.46(1) |
| | **$R_{WP}$(%)** | 3.31 | 3.22 | 2.93 | 2.97 |
| | **$R_F$(%)** | 5.12 | 8.05 | 7.70 | 7.98 |

## Figure captions

**Figure 1.** XRPD patterns for $CaTi_{0.6-x}Fe_{0.4}P_xO_{3-\delta}$ series (a) x = 0 and (b) x =0.025 sintered in the temperature range between 800 and 1400 ºC for 4 h.

**Figure 2.** XRPD patterns for $CaTi_{0.6-x}Fe_{0.4}P_xO_{3-\delta}$ series (x = 0, 0.025, 0.05 and 0.075) sintered at 1400 and 1200 ºC for undoped and P-doped compounds, respectively, for 4 h.

**Figure 3.** Rietveld plot of $CaTi_{0.575}Fe_{0.4}P_{0.025}O_{3-\delta}$ heated at 1200 ºC for 4 h.

**Figure 4.** XRPD patterns for $CaTi_{0.6-x}Fe_{0.4}P_xO_{3-\delta}$ series (x = 0, 0.025, 0.05 and 0.075) after firing at 800 ºC for 48 h under 5%$H_2$-Ar.

**Figure 5.** SEM and EDS image of surface of $CaTi_{0.6-x}Fe_{0.4}P_xO_{3-\delta}$ series (x = 0, 0.025 and 0.05) compounds.

**Figure 6.** Arrhenius plots of $CaTi_{0.6-x}Fe_{0.4}P_xO_{3-\delta}$ (x= 0-0.075) in (a) air and (b) 5%$H_2$-Ar.

**Figure 7.** (a) Current-voltage and power density curves of $P_{0.025}$/YSZ/$P_{0.025}$ symmetrical cell and (b) SEM image of the cross-section of the cell.

## Supplementary figure captions

**Figure S1**. Oxygen deficiency and average oxidation state of iron as a function of P-content, $CaTi_{0.6-x}Fe_{0.4}P_xO_{3-\delta}$ (x= 0-0.075).

**Figure S2**. XRPD patterns for $P_{0.025}$/YSZ mixture (1:1 wt.%) at room temperature and after firing between 800 and 1000 ºC in air.