

EFFECT OF THE CALCINATION TEMPERATURE ON THE OXYGEN EVOLUTION REACTION OVER Pr₆O₁₁ OXIDE

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ABSTRACT

The Pr₆O₁₁ oxide synthesized using the citrate sol-gel method was calcined at four temperatures 600, 700, 800 and 900 °C. The prepared powder was characterized by DTA-TGA, XRD, IR, SEM and cyclic voltammetry. The thermal analysis shows an endothermic peak at 765°C attributed the pure cubic phase. XRD diffraction pattern reveal that three phases Pr₂CO₅, Pr₄O₇ and Pr₆O₁₁ coexist at 600°C. At T ≥ 700°C, the secondary phases Pr₂CO₅, Pr₄O₇ disappear while the phase Pr₆O₁₁ becomes alone indicating the formation of the pure cubic phase. The microstructural analysis shows that powders are constituted from particles having different shape, size and are agglomerated. The electrocatalytic properties of samples were investigated using cyclic voltammetry. The better electroactivity performance was achieved for the lower calcined electrode.

Keywords: Pr₆O₁₁; Oxide; XRD; SEM; Cyclic voltammetry .

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INTRODUCTION

The reduction of costs, in terms of energy consumption and loading of precious metals for catalysts, is the main reason to search new anode materials with low cost and high performance in alkaline water electrolysis. To solve the questions of energy shortage and environment pollution, oxides compounds have been the focus in the fields of photo-catalysis



and photo-electricity conversion [1]. Among them praseodymium oxides are used as catalysts, catalyst carriers, promoters, stabilizers and higher electrical conductive materials [2,3]. Indeed it has been the subject of several works during the last decade. Borchert et al. [4] have synthesized nanostructured praseodymium oxides via four different methods, studied their catalytic properties for CO oxidation where the maximum of conversion reach ~ 95-96% at 550°C. Balachandran et al. [5] have coupled Pr₆O₁₁ oxide with ZnO and tested their performance as photocatalyst for the degradation of the dye. It has been shown that Pr₆O₁₁-ZnO exhibits higher photocatalytic activity compared to pure ZnO and Pr₆O₁₁ particles in the degradation of AV 7 dye. Later, Zinatloo-Ajabshir et al. [6] have prepared nanocrystalline praseodymium oxide by a novel facile precipitation route and characterize their optical and photocatalytic properties. Its use as a photocatalyst, the percentage of 2-naphthol degradation is about 100 after 12 min irradiation of UV light.

Anode overpotential is a major source of inefficiency in alkaline water electrolysis. The higher anode with high performance is an important goal in current electrolyzer development programs [7]. In this context, considerable works have been made to search new anode materials based on transition metal oxides. Despite the catalytic properties of Pr₆O₁₁ oxide, there is no reports on its use as anode for the oxygen evolution reaction (OER) in water electrolysis.

In our present work, Pr₆O₁₁ oxide has been synthesized by the citric acid sol-gel method and characterized for its physicochemical properties. The effect of the calcined temperature on the phase formation processes, particle size and electrochemical performance of this material is presented

2. EXPERIMENTAL

The nanocrystalline powder Pr₆O₁₁ was prepared by sol-gel method using lanthanum, iron, praseodymium nitrates as starting materials and citric acid as a complexing agent. The precursor salts La (NO₃)₃·6H₂O (sigma-aldrich), Pr(NO₃)₃·4H₂O (biochem), dissolved in ethanol, are added to a solution of citric acid with a molar ratio of (1:1) under vigorous magnetic stirring at 60-70°C for 2h. A green transparent solution was formed and becomes gradually viscous and later the amorphous gel was formed. To remove residual ethanol, the gel was dried in an oven at 100°C for 24 h. Thereafter, samples were calcined at 600, 700, 800 and 900°C for 6 h with a heating rate of 5 °C min⁻¹.

In order to estimate the calcination temperature, Pr₆O₁₁ powder is studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using on a

SETARAM LABSYS Evo with a heating rate of 10°C/min under atmospheric conditions. X-ray powder diffraction (XRD) patterns of the oxide catalysts were obtained at a sweep rate of 2° min⁻¹ on an X-ray diffractometer (BRUKER-D8) using CuK_α as the radiation (λ=1.542Å). The identification of crystalline phases were performed using data from the cards of JCPDS (International Center for Diffraction Data). FTIR spectra were recorded in air at room temperature with Frontier FTIR/FIR (Perkin Elmer) over the range (4000-400cm⁻¹). The transmission spectra were obtained on 1 mg of powdered sample dispersed in 100 mg of KBr pellet pressed under-vacuum. Moreover, the morphology of the samples was studied by using scanning electron microscope (SEM) VEGA 3 TESCAN.

The oxide catalysts were prepared by an oxide-slurry painting method. The powder was dispersed in ethanol by subsequent ultra-sonication of the mixture for 20 min and then stirred in an electrical oven at 90°C. A pure nickel plate was coated by a thin layer of oxide powders, then heating at 100°C for 2h in an electrical furnace.

Electrochemical study are carried using cyclic voltammetry (CV), in a conventional three-electrode single-compartment pyrex glass cell with a potentiostat-galvanostat (Model Parstat 4000). The reference electrode was Hg/HgO/1MKOH (0.098V vs SHE), Pt was used as a counter electrode. All potential values have been referred to this reference electrode.

Procedures followed in cyclic voltammetry (CV) The software used in measurements of CV is Versa-Studio.

3. RESULTS AND DISCUSSIONS

3.1 Thermal analysis

Figure 1 presents DTA and TGA curves of Pr₆O₁₁ powder with the heating rate 10°C.mn⁻¹ in the temperature range 25-900°C. Four distinct regions of weight losses are observed corresponding to the following temperature ranges: 100-160, 160-370, 370-560, 560-830°C.

In the first region, a weight loss associated to one large endothermic peak at ~149 °C, can be ascribed to the elimination of adsorbed or hydrated water. At higher temperatures 160-370 °C, two other reduction in weight are observed which are assigned to weak exothermic peaks at ca. 226 and 348°C, correspond probably to decomposition of nitrates and citrates into carbonates and decomposition of carbonates respectively. The third weight loss accompanied by two endothermic peaks at ~ 430 and 500 °C was possibly attributed to the decomposition of oxygen group carbonates [8]. The last region of weight loss (T ≥ 560 °C) was accompanied by an endothermic peak at 765°C corresponding to the formation of the oxide.

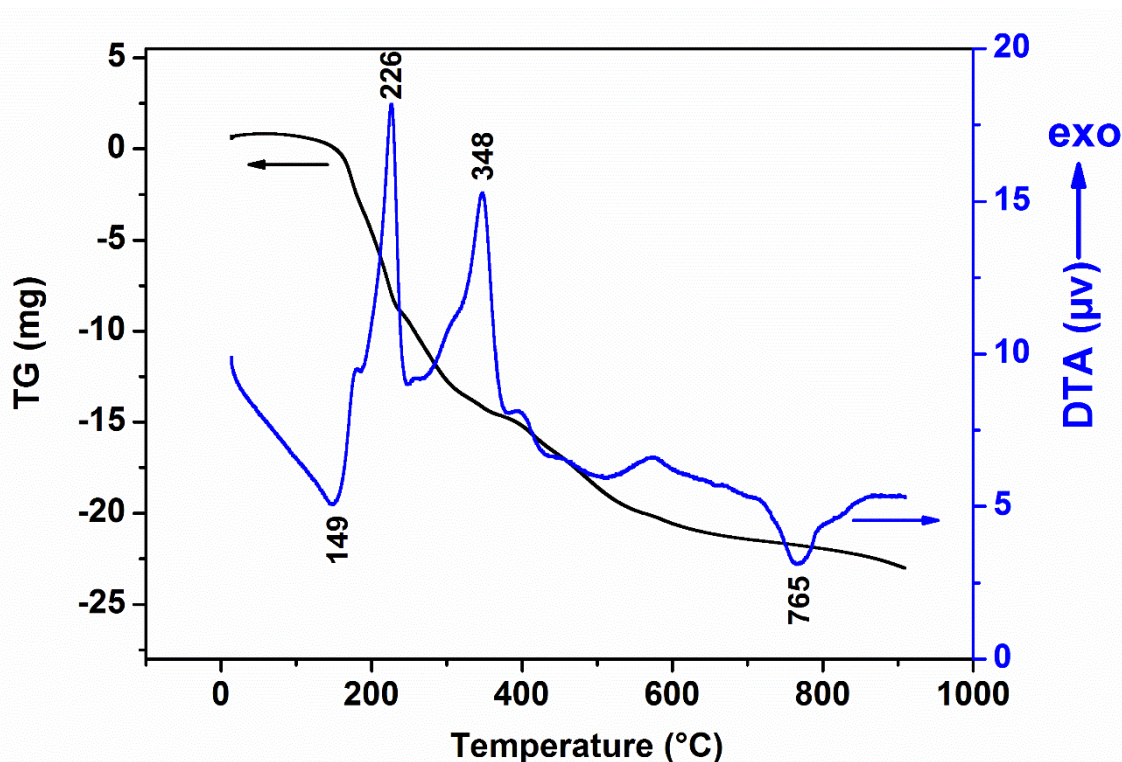


Fig.1. DTA-TGA of Pr₆O₁₁ powder with a heating rate of 10°C.mn⁻¹

3.2 X-ray Diffraction

Figure 2 presents X-ray diffraction patterns of Pr₆O₁₁ powder calcined at 600, 700, 800 and 900 °C. At 600 °C three phases coexist Pr₂CO₅ (00-025-0697), Pr₄O₇ (PDF : 00-065-6027) and Pr₆O₁₁ (00-042-1121) resulting from the degradation of precursors. The intensity of the two phases Pr₂CO₅ and Pr₄O₇ is higher than that of the cubic phase Pr₆O₁₁. At T ≥ 700 °C, the Pr₆O₁₁ phase becomes pure with high intensity of peaks which meaning that powders are more crystallized. Further heating at 800 and 900 °C, a slight shift of peaks to lower angles 2 θ was observed which is to say that powder are more sintered.

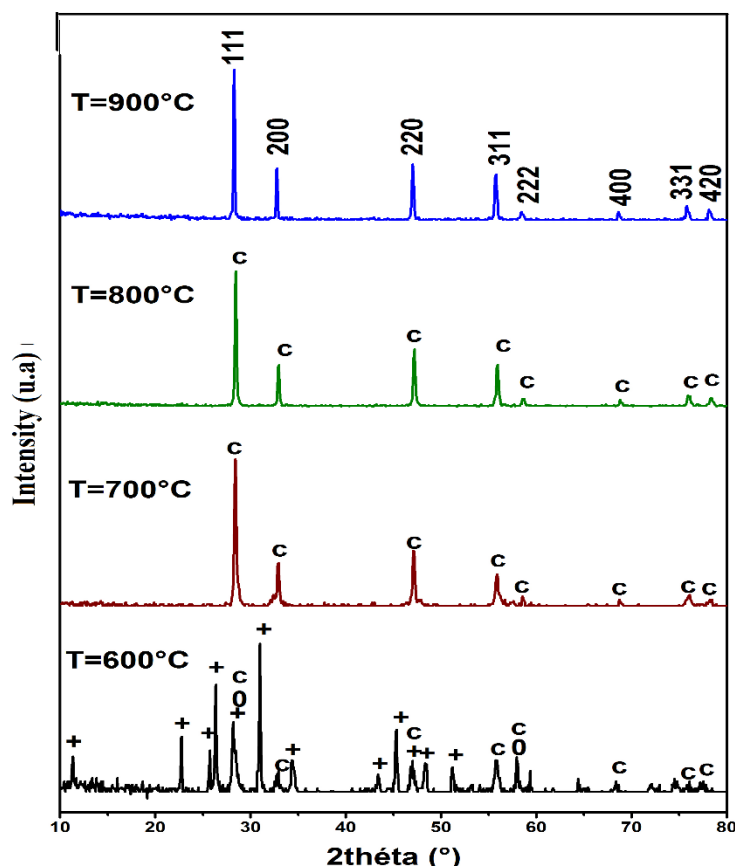


Fig.2. X-ray patterns of Pr_6O_{11} samples calcined at different temperatures : (+) Pr_2CO_5 , (0) Pr_4O_7 , (c) Pr_6O_{11}

The average crystallite size of particles calcined in the temperature range 600-900°C was calculated from the broadening of the XRD line width by using Debye-Scherrer equation (figure 3). For that, it was necessary to consider the peaks (111) of Pr_6O_{11} oxides. The oxides present an average crystallite size in the range of 16- 55 nm indicating that the fluoride powders prepared by the sol-gel method are composed of nanometric particles. It is observed that the crystallite size increases with increasing temperature. The same result was also found previously [9]. It has been shown that SnO_2 particles synthesized by a conventional precipitation method increase with the increase of calcination temperature. The rapid increase of the crystal growth with increasing in the calcination temperature can be probably ascribed by more agglomerated crystals.

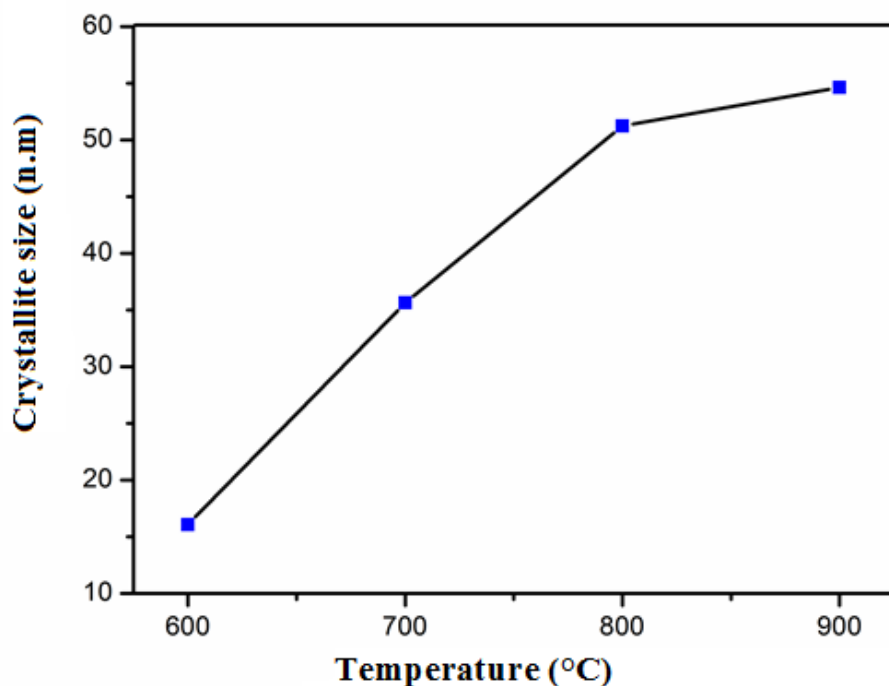


Fig.3. Crystallite size of samples calcined at different temperatures

3.3 Infrared spectroscopy

IR spectra of Pr_6O_{11} samples calcined at 600, 700, 800, 900 °C are presented in figure 4. At 600°C, six bands are observed at ~ 600, 751, 856, 1093, 1382 and 1468 cm^{-1} . The three bands observed at 1093, 1382 and 1468 cm^{-1} can be probably attributed to monodentate carbonates [4]. The weak band situated at 602 cm^{-1} is possibly assigned to the stretching vibration of δ (Pr–O–Pr) mode [10]. The two other peaks at 751 and 856 cm^{-1} corresponds to the stretching mode vibrations of Pr–O [11]. At $T \geq 700^\circ\text{C}$, the band at ~ 600 cm^{-1} becomes more intense which is in agreement with the XRD results showing a pure cubic fluorite phase in this temperature range.

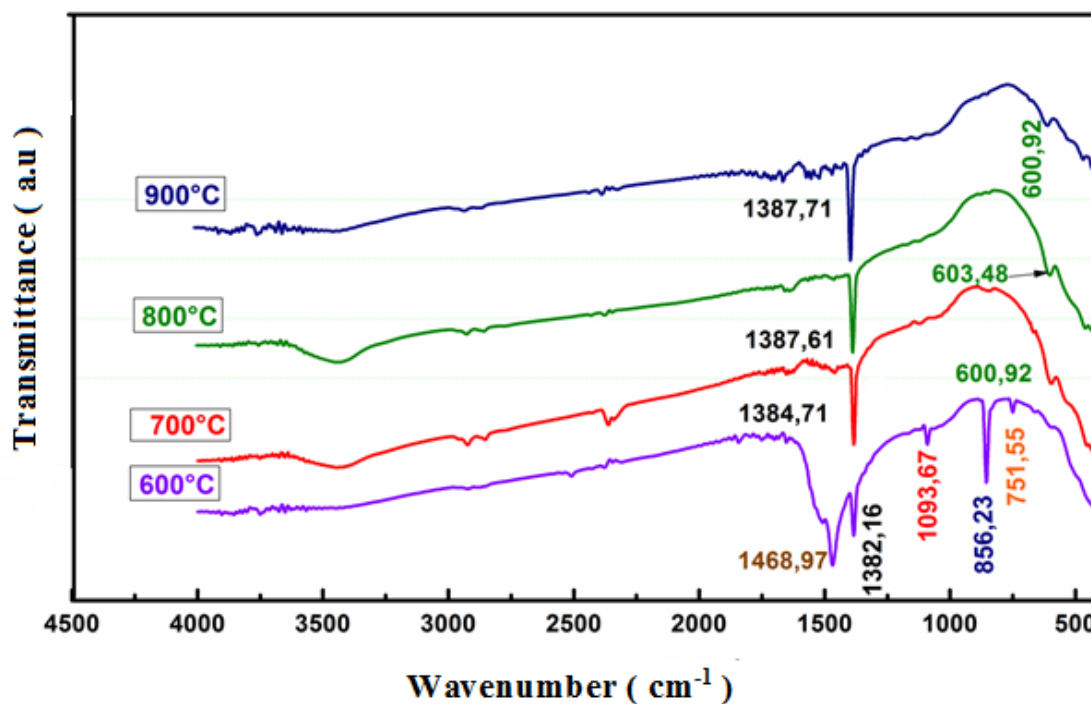


Fig. 4. Infrared spectra of Pr₆O₁₁ powders calcined at different temperatures

3.4 Scanning electron microscopy

Figure 5 presents micrographs of Pr₆O₁₁ samples calcined at 700 and 900 °C. Powders are constituted of particles strongly agglomerated while their sizes and shapes are not well defined. The pore sizes are too low. This uncontrolled agglomeration of powders due to attractive Vander Waals forces can also give rise to microstructural inhomogeneity. Differential stresses that develop as a result of non-uniform drying shrinkage are directly related to the rate at which the solvent can be removed and thus highly dependent upon the distribution of porosity. Moreover, the surface morphology indicates a dense microstructure of these copper-doped ceramics, which is probably due the particles that have a high tendency of agglomeration with interconnected structure. Similar results are previously found [12]. It has been shown that the use of ethanol as solvent allows interactions between particles which leads during drying to the formation of chemical bonds.

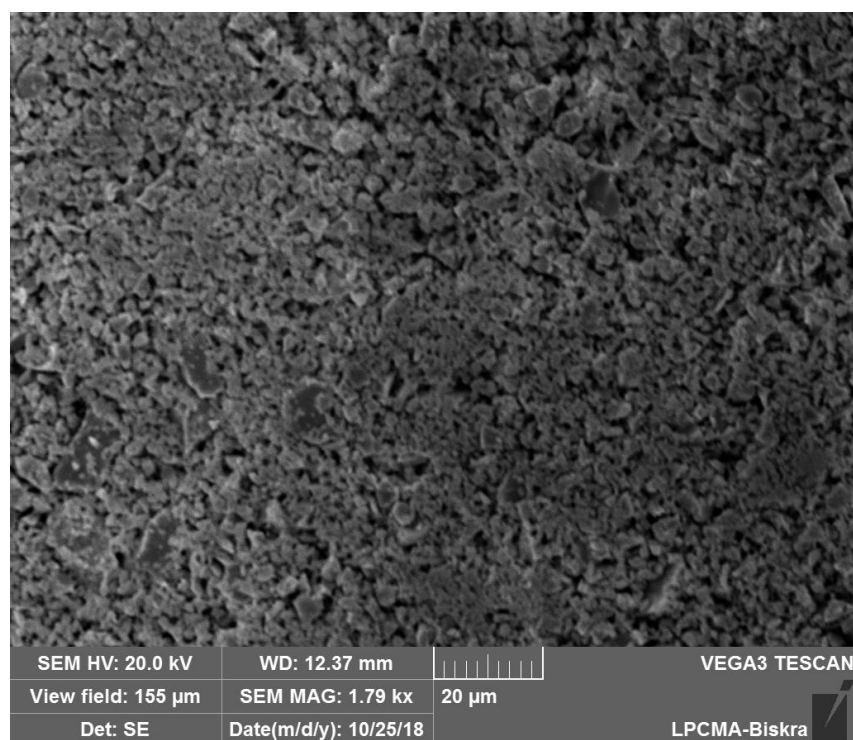
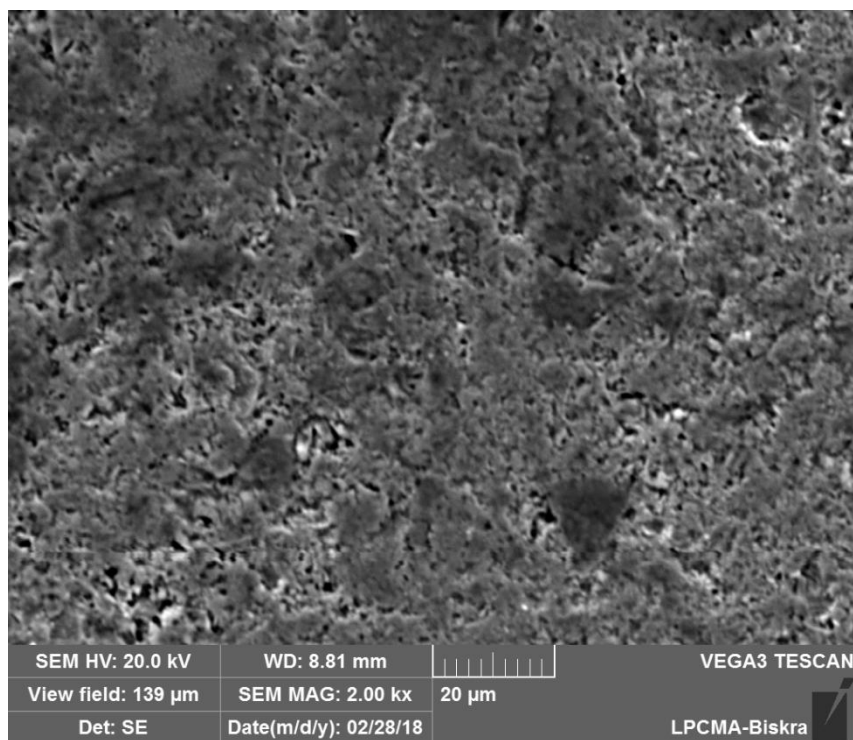


Fig.5. Micrographs of Pr_6O_{11} samples calcined at 700 (A) and 900 °C (B)

3.5 Electrochemical properties

Figure 6 presents cyclic voltammograms of Pr_6O_{11} electrodes calcined at 600, 700, 800 and 900 °C in 1M KOH. Similar curves are obtained for forward and reverse scans. For the forward scan, a weak redox peak corresponding to $\text{Ni}^{2+}/\text{Ni}^{3+}$ is observed in the potential range 0.45-0.55 V followed by the oxygen evolution reaction up to 1.1 V, where the onset potential is 0.42 V for samples calcined at 600 and 700°C while it is higher slightly at ~ 0.435 V for that calcined at 800 and °C. For the reverse scan, the same peaks appear in all cases but with a small shift to lower potential. The current density at 0.7 V ($\sim 5 \text{ mA}\cdot\text{cm}^{-2}$) is higher for the sample calcined at 600°C compared to the other electrodes indicating clearly the influence of the calcination temperature on the oxygen evolution reaction. Similar behavior was also found for $\text{IrO}_2\text{-Ta}_2\text{O}_5$ anodes used in oxygen evolution reaction [13]. It has been reported that the sample calcined at low temperature exhibits the higher performance for the oxygen evolution reaction which is attributed to the surface morphology and a change in active surface area. This result is also in good agreement with previous work on the electrocatalytic performance of ruthenium oxide [14] and IrO_2 oxides used as anodes catalysts in water catalysis [15]. It has been shown that RuO_2 particle size increases and the material becomes more crystalline with increase of calcining temperature, leading to lower electrochemical active surface and higher electronic conductivity. On the other hand, the results of IrO_2 electrodes show that the active surface decreases with increasing annealing temperature. The capacitance decreases to about 25% of the non-annealed sample when annealing at 540°C. The decrease in voltammetric charge after annealing can partly be due to area reduction associated with particle growth and coalescence and partly due to the dehydration of the oxide with stronger oxide bridge bonding.

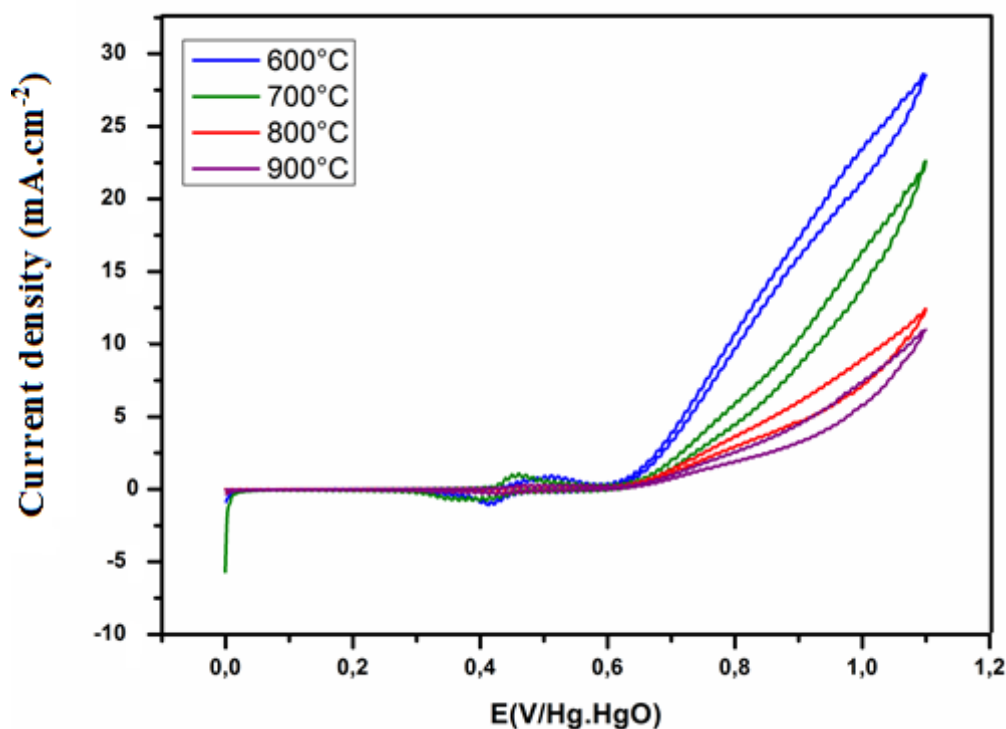


Fig.6. Cyclic voltammograms of Pr₆O₁₁ electrodes calcined at different temperatures in 1M KOH

4. CONCLUSION

The effect of calcination temperature on the structural and electrochemical properties of Pr₆O₁₁ electrodes calcined at 600, 700, 800 and 900 °C in alkaline media was explored. XRD patterns exhibit three phases Pr₂CO₅, Pr₄O₇ and Pr₆O₁₁ at 600°C resulting from the degradation of precursors. At higher temperature $T \geq 700$ °C, the Pr₆O₁₁ phase becomes pure with high intensity of peaks which meaning that powders are more crystallized. Three infrared bands situated at 602, 751 and 856 cm⁻¹ are observed and confirm well the XRD results. Cyclic voltammetry measurements show that the sample calcined at lower temperature exhibits the higher performance for the oxygen evolution reaction in 1M KOH. Future studies could investigate the association between the influence of calcination temperature and the doping with transition metals on the electrocatalytic performance of these materials for water electrolysis in alkaline media.

5. REFERENCES

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