Electrochemical Behaviour of $YBaFe_2O_{5+\delta}$ in Alkaline Electrolyte

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Abstract: In this paper we are presenting the electrochemical investigation of mixed oxide YBaFe₂O₅ in alkaline electrolite during oxygen insertion/release. Firstly, mixed oxide morphology was studied by scanning electron microscopy and also by using X ray diffraction. Electrochemical behaviour of studied compound has been studied by cyclic voltammetry technique. Based on obtained results were identified all the electrochemical processes occurring at interface mixed oxide / electrolyte.

Keywords: Mixed oxide YBaFe₂O₅, electrochemical behaviour of YBaFe₂O₅, cyclic voltammetry

1. Introduction

The high demand for environmental friendly power sources transform fuel cells in one of main competitors. From this point of view solid oxide fuel cells represent one viable alternative due to high electrical generating efficiency [1], which can be coupled with heat recovery, multi-fuel capability and also simplicity of the system [2, 3]. However, in classical SOFC the high conductivity of used solid electrolyte and also high efficiency of the system can be achieve when the fuel cells is operated around 1000°C [3]. High operation temperature leads at several issues like thermal stress [3], long-term stability of the components, cost of materials, ... [2]. Some of these issues can be overcome by lowering operational temperature, but for that is necessarily to develop new type of electrodes and also new solid electrolyte. During last period the effort of different scientist have been focused on the development of intermediate temperature solid oxide fuel cells [2]. High demand for intermediate temperature SOFC leads at development of electrodes with better electrocatalytic activity around 600°C [4]. One option for these electrodes is represented by Y-112 mixed oxides due to their special layer structure [5] which is responsible for valuable properties of this class of compounds: high oxygen conductivity [5] which is leading at high area for oxygen reaction coupled with high oxygen surface exchange coefficients [4].

2. Experimental

YBaFe₂O₅ mixed oxide was prepared using solid-state reaction by mixing the following precursors Y_2O_3 (Aldrich 99.99%), BaCO₃ (Aldrich 99.99%) and Fe₂O₃ (Aldrich 99.99%) in accordance with the stoichiometric cation rate. In first stage the reaction mass was heated at 1000°C in order decompose the carbonates. After that, the reaction

mass was cooled at room temperature, grinded and reheated at 1200°C for at least 48 h. Later, obtained powder was pressed into circular electrodes fried in air at 1200°C for minimum 48 h [6-8].

Surface morphology of synthesized perovskyte has been characterized by scanning electron microscopy (SEM) using a FEI Quanta 200 microscope. The structure of YBaCo₂O₅ compound was checked by X-Ray powder diffraction (XRD) (Philips X-pert Pro). All electrochemical studies were performed using and potentiostat/galvanostat Autolab 302N equipped with electrochemical impedance spectroscopy module. Used electrochemical cell was equipped with two graphite counter electrodes positioned symmetrically against the working electrode (made from YBaFe₂O₅ disk with active surface of 0.5 cm⁻²) and also a Ag/AgCl electrode used as reference. All electrochemical data presented in this work are expressed versus the reference electrode. A 1 mol L⁻¹ KOH solution was used as electrolyte during all electrochemical studies.

3. Results and Discussion

3.1. Physical characterization

SEM images obtained for Y-112 disk electrode studied into this work are presented in Fig. 1. Analyzing the SEM pictures presented a porous structure attributed to crystallite agglomeration can be observed. Large pore amount observed leads to higher specific surface area with channels which favors the oxygen adsorption/desorption process.

XRD diffraction spectra was recorded for 2θ range between 0° and 100° and is presented in fig. 2. All peaks from recorded XRD spectra were identified using the ICC data base and from that can conclude that the obtained is the desired YBaFe₂O₅ mixed oxide. After that the elemental composition of mixed oxide was confirmed by energy dispersive X-Ray analysis (EDAX), and the obtained results are presented in Fig. 3.



(a)

(b)

Figure 1. SEM micrographies obtained for YBaFe2O5 electrode surface at 6000x (a) si 3000x (b)



Figure 2. XRD spectra recorded for YBaFe2O5



Figure 3. YBaFe₂O₅ EDAX spectra

3.2. Electrochemical characterization

From preliminary test can be observed that the different peaks associated with electrochemical process taking place at interface mixed oxide electrolyte can be separate only at lower scan rate. Cyclic voltammograms recorded at a scan rate of 100 mV s⁻¹ are presented in Fig. 4. Analyzing the data presented in Fig. 4 can be observed on the forward scan the appearance of a clear plateau (1) which can be associated with the oxidation of mixed oxide. When the electrochemical process is conducted at higher potentials a change in curve slope was observed, associated with oxygen evolution reaction. On the backward scan a small peak appear around 0.4 V, which can be correlated with two different processes taking place concomitant onto the electrode surface: reduction of remanent oxygen and also reduction of iron ions.



Figure 4. Cyclic voltammograms recordet in KOH 1M, dE/dt=100 mV/s

In Fig 5 is presented the cyclic voltammogram obtained when the scan rate was 5 mv s⁻¹. From this image can conclude that the electrochemical processes taking place at interface can be separated. On this cyclic voltammogram are seen five different peaks. Appearance of peak 2 around 0.45 V can be associated with the oxidation of Fe(II) ions (Fe(II) \rightarrow Fe(III) + e⁻). An increase of current (labeled as peak 3) can be observed at higher potentials, and this peak was associated with oxygen evolution reaction. On the backward scan reduction of remanent oxygen lead to appearance of a cathodic plateau labeled as 4. When the electrode potential was shifted at much negative values, a pronounced cathodic peak (5) associated with the reduction of Fe(III) ions (Fe(III) \rightarrow $Fe(II) + e^{-}$ appears around 0.28 V. At much negative potentials, a new oxidation peak appears around 0 V due to the oxidation of superficial adsorbed hydrogen.



Figure 5. Cyclic voltammograms recordet in KOH 1M, dE/dt=5 mV/s

4. Conclusion

Analyzing the results obtained by cyclic voltammetry we can say that mixed oxide electrode is sensitive at anodic and also cathodic polarization. Presence of peak at 0.45 V on the recorded voltammograms was associated with the oxidation of superficial Fe(II) ions, followed by oxygen oxygen evolution reaction.

Presence of cathodic peak at 0.28 V has been associated with the reduction of Fe(III) ions. By similarity with other perovskytes is expected that the oxidation process consist in oxygen insertion into the mixed oxide structure which is leading at a compact structure. Difference between oxidation and reduction peaks maxima is a direct consequence of mixed oxide compaction during oxidation which is imposing a partial irreversible character for oxidation process.

In a future paper we will present a complete characterization of the fully oxidized phase.

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