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Manufacture and Characterisation of Novel Cathodes for Solid Oxide Fuel Cell

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Abstract

The solid oxide fuel cell (SOFC) is a device of energy conversion which has high efficiency and very low green house emission. In this work, the anodes are made from composite materials - typically Nickel in yttria stabilized zirconia (YSZ) while cathodes are made of lanthanum strontium manganate (LSM). The aim of this research is to investigate and manufacture the cathode of an SOFC by using a novel electroless co-deposition of nickel, YSZ and LSM onto a ceramic substrate. Initially, a cathode for a traditional (higher temperature) SOFC is manufactured using LSM powder in a nickel electroless bath. The effect of orientation (horizontal and vertical) of the substrate is investigated. The second stage of the project is to manufacture a cathode for intermediate temperature SOFCs by using a Nickel/LSM/YSZ composite. For this, the substrate is placed horizontally in the electroless bath. Finally, the evaluation of the experimental work is carried out by examining the coating using optical microscopy, electron microscopy and energy dispersive X-Ray analysis. The results from the experimental work carried out to manufacture these cathodes are found to be encouraging. For the cathode used in the higher temperature SOFCs, successful co-deposition of nickel and LSM is achieved. Additionally, the substrate coated in the horizontal position shows a higher percentage of LSM powder deposited than the substrate coated in the vertical position. However, the horizontally positioned substrate is found to be less uniform in nature compared with the vertically positioned one. Furthermore, the thickness coated in the vertical substrate is about 22µm while the thickness of the horizontal one is about 5µm. For the intermediate temperature SOFC cathode, successful co-deposition of nickel and LSM/YSZ is achieved.

Keywords: SOFC; Yttria stabilized zirconia; Nickel; Orientation, electroless co-deposition.

1. Introduction

In modern civilization, the air pollution is causing major global problem due to the excessive use of fossil fuel. The solid oxide fuel cell (SOFC) is a device of energy conversion which has high efficiency and very low green house emission. Therefore, by using SOFC techniques this can lead to minimize the greenhouse gases contamination and enhance the environment [1]. Similar to other type of fuel cells, SOFC requires the fuel such as hydrogen, and oxidant reactants such as oxygen or air to electrochemically react at high temperature and generate electrical energy [2]. SOFC has very good advantages; for example, it uses non precious catalyst metals, fuel flexibility, and high waste heat quality for applications of heat cogeneration as well as, solid electrolyte and relatively high power output. However there are some disadvantages of high temperature materials, sealing problems and relatively high cost of component fabrications [3]. However, the SOFC is a system has some limitation, for example; the cost of the materials and manufacturing process [2]. The SOFC history started at the end of 19^{th} century by Nernst who proposed that the electrolyte could be made from solid materials.

Nernst fuel cell model used a heater which makes the fuel cell produce electrical current by implementing pure metal solid oxides which their resistance could be reduced by adding certain amounts of other oxidants [4]. The most common mixture of solid oxide electrolyte is zirconia (ZrO_2) with a little amount of yttria (Y_2O_3) (YSZ) [5]. Later, Baur and Preis in 1937 introduced the first working SOFC using ceramic fuel cell at temperature around 1000^{o}C by using electrolyte of stabilized zirconia (85% zirconia and 15% yttria) and magnetite and coke as a oxidant and fuel, respectively [6]. Generally, the performance of SOFC can be improved by reducing the electrolyte thickness, and the intermediate temperature of SOFC (ITSOFC). For good SOFC performance, the YSZ electrolyte should be free of porosity to prevent the gases filtering between the electrodes; it must be thin and uniform to minimize the ohmic loss. Also it must have high conductivity to the oxygen ion which may reach to the unity while electrons transport number should be around zero [7]. YSZ mechanical stability is improved by adding a small amount of alumnia, and zirconia of tetragonal phase is added to strengthen the structure of the electrolyte and enable of making thinner materials. However, recently, there are many reported about improving the SOFC cathodes [7, 8]. However, there are two types of materials commonly used to manufacture the interconnection: ceramic and metallic alloys [1]. In high temperature operation, the SOFC are usually implement cathode type of (LSM) lanthanum strontium manganate perovskite oxide which it's operating temperature above 900^{o}C. LSM materials have appropriate characterises; for example, high electrical conductivity, good thermal compatibility with the other components of SOFC. Moreover, LSM thermal expansion coefficient is nearly similar to that of electrolyte yttria–stabilize. In the initial stages, LSM1 (1.54 µm) electrode shows good values in the activities regarding the charge-transfer resistance [9]. Both Kenjo and Nishiya are the first who have attempted to modify the LSM-based cathode [10]. There are also other studies focused on enhancing the conductivity of the oxide ion of the electrolyte by improving and optimizing the materials used, for example; lanthanum gallate-based oxides which partly changed by magnesium, YSZ, strontium and ceria partly changed by gadolinium, samarium, yttrium and calcium [1]. LSM and YSZ powders used with the same grain sizes, the optimum ratio of LSM/YSZ mass were measured at 50/50 [11, 12]. Commonly, the cathodes have been manufactured by various preparation methods, for example; tape casting, screen-printing and chemical/physical vapour deposition. However, the techniques are usually very expensive or they are long time of processing [13].

This research proposes another solution to reduce the cost of SOFC. This will be implemented by using a novel method to manufacture lanthanum strontium manganate/nickel cathodes for solid oxide fuel cells using electroless deposition onto alumina. The benefits of using low operating temperature solid oxide fuel cell reduces the interfacial reaction between electrolyte and the electrodes which may lead to degradation performance, minimize the damage due to the thermal expansion mismatch at high operating temperature, minimize the processing cost and provide wide variety to the material selection. The aim of this research is to carry out experimental work procedures to manufacture cathode of SOFC by using electroless coating of nickel on electrolyte alumina (Al_2O_3). In this work, the first stage was preparing the traditional cathode of SOFC which operates at high temperature 1000°C by using Lanthanum strontium manganate (LSM) powder. The substrate was put in a bath of electroless coating in two positions horizontal and vertical directions. The second stage of this research is to prepare a cathode of intermediate temperature of SOFC which operates at low temperature at range of (600-700°C) by using LSM/YSZ composite electrodes. In this stage the substrate was put in electroless coating bath in one position of horizontal direction.

2. Material and Methods

2.1. Materials

There are four types of materials used in pretreatment step, Cuprolite X96 DP, Uniphase PHP Precatalyst, Uniphase PHP Catalyst and Niplast AT 78. The sensitising and activator solution were manufactured by AlfaChimici under the tradename of uniphase PHP. Electroless coating materials consists of substrate alumina (Al_2O_3) and Lanthanum strontium manganate (LSM) $(La_{0.8}Sr_{0.2})_{0.95}MaO_3$ powder used in this study which was manufactured by Praxair, and had particle size distribution d10-0.8µm d50-1.2µm d95- 4µm, and surface area of (8.96 m^2/g). Electroless nickel (Ni) chemicals were manufactured by Schloetter Company Ltd under the Tradename of Slotonnip 2010, and produced a bright mid-phosphorous (6-9%) nickel deposit. The 8% Yttria stabilized zirconia (YSZ) powder used in this study was manufactured and supplied by Unitec Ceramics Ltd, and had a nominal particle size of 2μm.

2.2. Methods

The first stage was preparing the traditional cathode of SOFC which operates at high temperature 1000 °C by using Lanthanum strontium manganate (LSM) powder. The electrolyte was put in a bath of electroless coating in two positions horizontal and vertical directions (first and second substrate). The second stage of this research is to prepare a cathode of intermediate temperature of SOFC which operates at low temperature at range of (600-700°C) by using LSM/YSZ composite electrodes. In this step the electrolyte was put in electroless coating bath in one position of horizontal direction (third substrate). Finally, the evaluation of the experimental work is carried out by examining the coating by EDXA (Energy Dispersive X-Ray Analysis) to measure the possibility of manufacturing the cathode by using electroless nickel coating by verify of the powder existence on the electrolyte.

2.2.1. Pre-treatment for alumina

The alumina substrate was rinsed with deionised water after each washing steps, Firstly use 150 ml of Cuprolite X96 which is taken into a beaker and heated to 60 ºC then insert the substrate in the baker for 15 min. Followed by using 150 ml of Uniphase PHP Pre-catalyst is taken into a beaker and insert the substrate in the beaker at room temperature and at 35 ºC for 15 min. Lastly, 150 ml of Niplast AT 78 is taken into a beaker and heated to 35 ºC then insert the substrate in the beaker for 15 min.

2.2.2. Electroless Coating

Electroless coating is a process of deposition certain materials on a substrate without use of external electrical power. The process is simply implemented by immersing the substrate need to be plate in plating bath to develop an adherent coating. Most metals and non-metals can be plated; therefore, this is the big advantages for this method. This method gives typical deposition rates from 12.5 to 20 μm per hour. Nickel is the most popular metal to be deposited by this process. Electroless nickel deposits are dense, hard, and very effective against corrosion, friction properties and adheres to most metals very well due to both intermetallic and mechanical bonding to the substrate [1]. Electroless coating was done for three substrates; the first substrate was inserted in bath of electroless nickel coating with LSM powder in vertical direction while the second substrate was inserted in a similar bath but in horizontal direction. The third substrate was inserted in bath of electroless nickel coating with LSM/YSZ powder in horizontal direction. Then, the procedures of electroless nickel coating with LSM powder operation for the first and the second substrate were summarized as shown in Figure (2.1). Then, the procedures of electroless nickel coating with LSM/YSZ powder operation for the third substrate were summarized as shown in Figure (2.2).

3. Results and Discussion

The results of the experimental work can be confirmed by examining the coating to verify the existence of the powder on the electrolyte. This process is done by EDXA to measure the possibility of manufacturing the cathode by using electroless nickel coating. EDXA theory of operations based on using a beam of scanning electron microscope which strokes the samples, where the atomic structure changes due to emitting X-rays.The results were clearly analysed by energy-dispersive spectrometers and a graph was yielded which exactly indicates the distribution of the amount of elements [14]. To measure the thickness of the coating resulted for the first and the second substrate which were coated by LSM powder using electroless nickel technique. Both samples were cut using a simple method by making a scratch on the surface of substrate by using a tool has diamond tip. Then, the substrates were hold tight between two rulers on one side very close to the scratch and apply pressure by hand to break the substrate along the scratch which has been made. Then mount the samples into Epofix. Clean the mould and spray with lubricant to ease the release the sample from the mould. After that the sample inserted in the middle of the mould. Then pour Epofix in the mould carefully. Put the mould into Epovac for 5 minutes under vacuum about 200 mbar. Then leave the sample in the Epovac for 8 hours. After that both sample well be grinded and polished. Then apply sputter coating on the samples to be electrical conductive to be tested by EDXA to measure coating thickness. Initially, the powder (LSM) and the substrate (Al_2O_3)

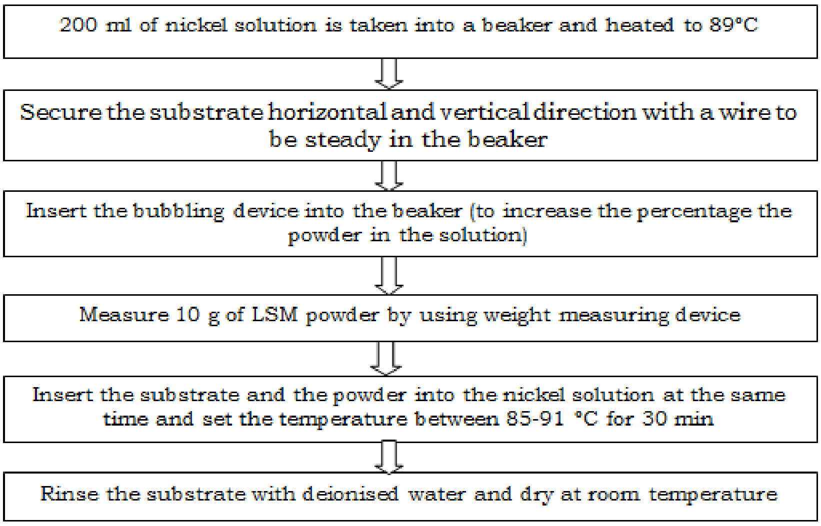


Figure 2.1: The procedures of electroless nickel coating with LSM powder operation for the first and the second substrate.

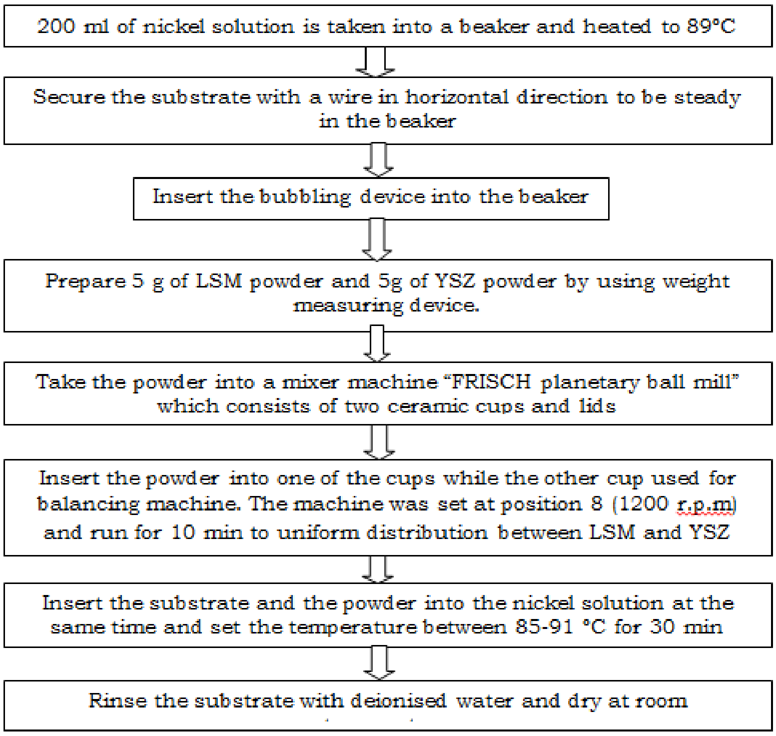
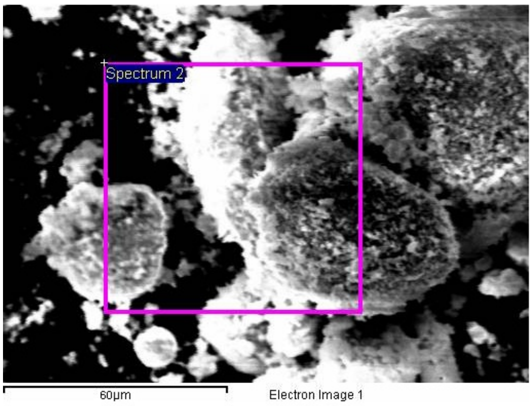
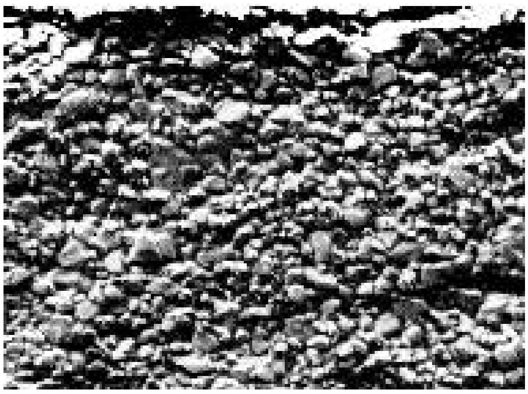


Figure 2.2: The procedures of electroless nickel coating with LSM/YSZ powder operation for the third substrate.

were tested by using EDXA. The powder was put in adhesion carbon tap. Then, the result shows that the powder has different size of the particles. This demonstrated in Figure (3.1a). While the electrolyte shows very close particles (see Figure (3.1b)). In the first substrate which was inserted in horizontal direction in the bath of electroless nickel coating with LSM powder is likely to have pores in the coating created. This can be proved in the spectrum chart Figure (3.2a). This can be noticed from the big peak of aluminium (the weight percentage is about 48%, Figure (3.2b)).



(a)



(b)

Figure 3.1: . Shows the microstructure of (a) the powder (LSM) by using EDXA (b) microstructure of substrate (alumina) by using SEM.

In the second substrate which was inserted in vertical direction in the bath of electroless nickel coating with LSM powder is likely to have pores in the coating created (Figure (3.3a & b)). This can be proved in the spectrum chart Figure (3.4a-d). This can be noticed from the big peak of aluminium (the weight percentage is about 45%, Figure (3.4d)). By comparing the first and the second substrate, the first substrate which coated in horizontal positions shows more percentage of powder (LSM) than the second substrate which coated in vertical position. This may likely to be due to the horizontal layout of the substrate allowing for more chance for the powder to contact the lower surface of the substrate. Moreover, it can be noticed that the substrate will divide the bath in two parts making the lower side is richer of the coating powder. Therefore, the lower side of the substrate will be richer with the powder than the upper side. However, the first substrate which coated in horizontal position has non uniformed coating while the second substrate which coated in vertical position has uniformed coating. This may likely to happen because in the second substrate of the vertical position there are more space to make homogeneous solution (powder LSM and the nickel solution) allowing for good uniform depositions. Furthermore, the size of the thickness coated in the second substrate is about 22.4 µm while the thickness of the first substrate is about 5.2µm.

In the third substrate which coated horizontally by electroless nickel with LSM/YSZ powder, this process was carried out and verified that this method can be applied to manufacture the cathode for SOFC in intermediate temperature (Figure (4.1a)). In addition, the peaks and the weight percentage of elements exist in electroless nickel coating with LSM/YSZ powder for horizontal substrate by using EDXA were presented in Figure (4.1b).

4. Conclusion

In this research, a successful experiment was carried out to manufacture a cathode to be used in a high and intermediate temperature solid oxide fuel cell. For the cathode which is used in the high temperature solid oxide fuel cell, co-deposition of nickel and LSM was successfully achieved. This was experimented by putting two different samples of substrate in two different directions, namely vertical and horizontal. The first substrate is coated in the horizontal position which showed a greater percentage of LSM (compared with nickel) than the second substrate which was coated in the vertical position. However, the horizontally positioned substrate was of less uniform coating while the vertically positioned substrate was coated more uniformly. Furthermore, the size of the thickness coated in the

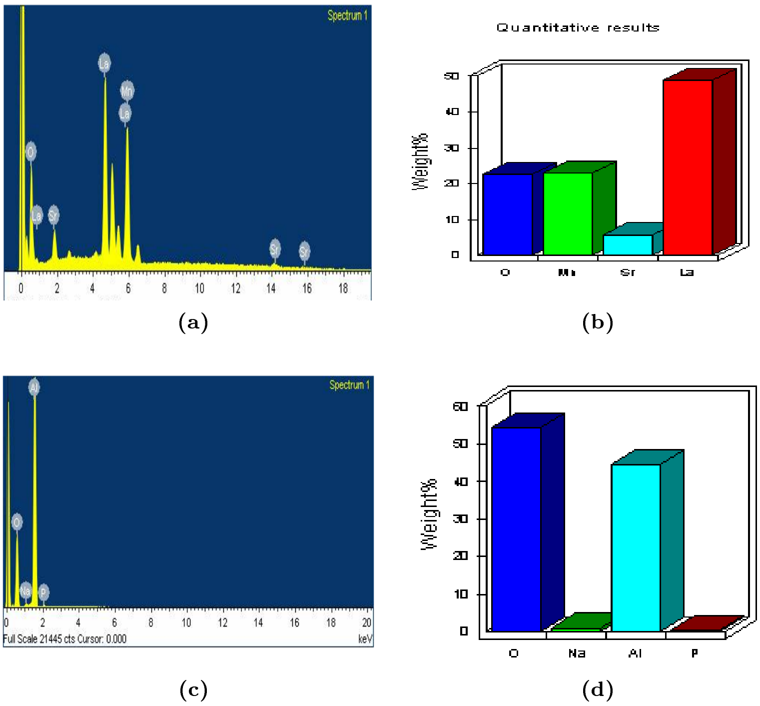


Figure 3.2: Shows (a) the peaks, (b) the weight percentage of the elements in the powder (LSM), (c) the peaks and (d) the weight percentage of the elements in the substrate (alumina) by using EDXA.

vertical substrate was greater (22.4 µm) than the thickness of the horizontal substrate (5.2µm). However, it is recommended that to increase the thickness of the coating, the substrate should stay longer in the bath of the electroless deposition. The intermediate solid oxide full cell – which is a mix of LSM, YSZ and nickel was also successfully deposited. The Yttria stabilized zirconia (YSZ) powder used in this study had a nominal particle size of 2µm. However, it is recommended to use particles with different sizes of YSZ to make the cathode more porous this to increase the performance of the cathode.

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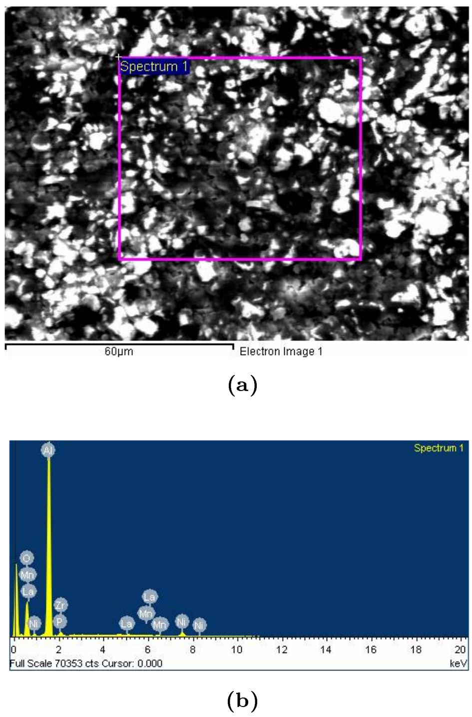

Figure 4.1: Shows (a) the microstructure of electroless nickel coating (b) the peaks and the weight percentage of elements exist in electroless nickel coating with LSM/YSZ powder for horizontal substrate by using SEM.

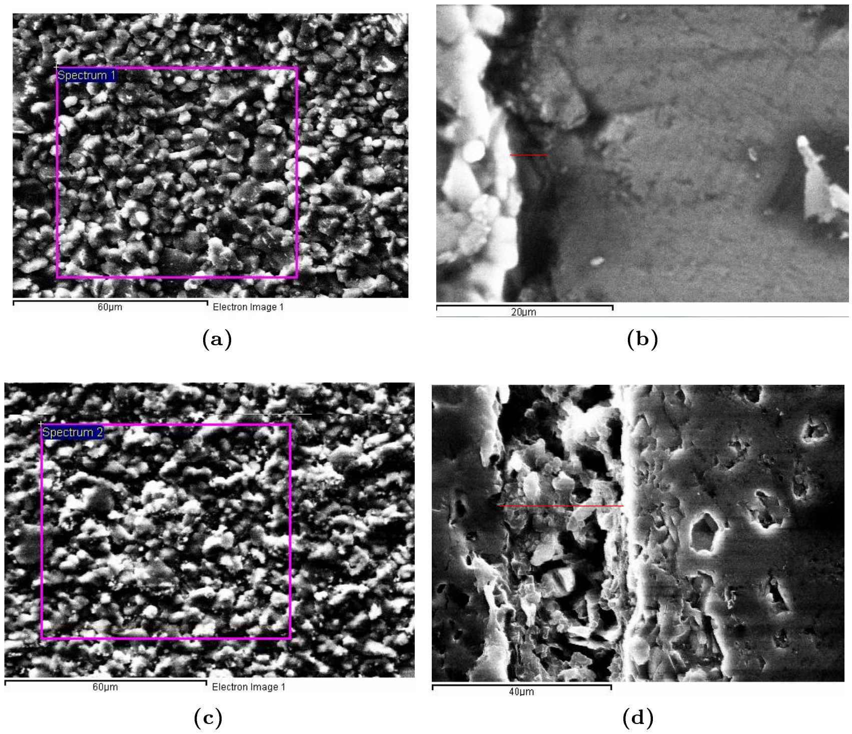

Figure 3.3: Shows (a) the microstructure, (b) the thickness of electroless nickel coating with LSM powder for horizontal substrate, (c) the microstructure and (d) the thickness of electroless nickel coating with LSM powder for vertical substrate by using SEM.

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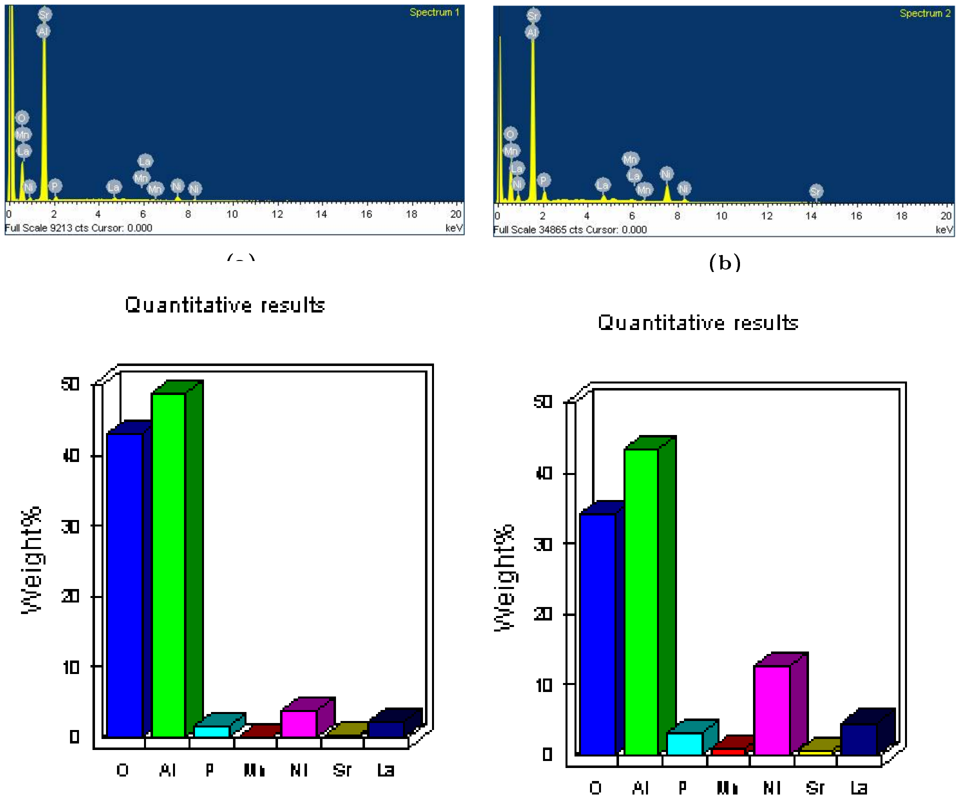

Figure 3.4: Shows (a) the peaks, (b) the weight percentage of elements exist in electroless nickel coating with LSM powder for horizontal substrate (c) the peaks (d) the weight percentage of elements exist in electroless nickel coating with LSM powder for vertical substrate by using EDXA.

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