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Study of Pani Nanofibers Supported Pt Catalysts for Fuel Cell

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Abstract In this study, the preparation and characterization of polyaniline nanofibers supported platinum (Pt) as novel cathode catalyst for Proton exchange membrane fuel cells (PEMFCs) are presented. This paper aims to study the production of polyaniline nanofibers (PANI-NFs) at different aniline/oxidant ratios via interfacial polymerization method. PANI-NFs supported Pt catalysts (Pt/PANI-NFs) were synthesized by an ethylene glycol reduction method. The synthesized PANI support material and Pt/PANI catalyst are analyzed using several methods on Scanning Electron Microscopy with LXRf system (SEM), X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR).

Keywords: Proton exchange membrane fuel cell; Alternative support material; Platinum; Polyaniline nanofiber; interfacial method

Исследование полианилиновых нано-волокон, поддерживающих платиновые катализаторы для топливных элементов

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Аннотация В этой работе рассмотрены вопросы изготовления и характеристики полианилиновых нано-волокон, поддерживаемых платиной (Pt), как новый вид катода катализатора для протон-обменных мембранных топливных элементов. Целью данной работы является изучение изготовления полианилиновых нано-волокон (ПАНИ-НВ) по методу межфазовой полимеризации при различных соотношениях анилина /окислителя.

ПАНИ-НВ поддерживающие платину (Pt) катализаторы (Pt/ПАНИ-НВ) синтезированы методом выделения этиленгликоля. Синтезированный ПАНИ- поддерживаемый материал и катализаторы Pt/ПАНИ изучены с помощью различных методов, таких как растровая электронная микроскопия, рентгеновская дифракция и инфракрасная спектроскопия с фурье преобразованием.

Ключевые слова: Протон-обменные мембранные топливные элементы; полианилиновые нано-волокна; межфазовый метод

I. Introduction

Proton exchange membrane fuel cells (PEMFCs) are highly attractive power sources for a variety of applications, due to their high energy efficiency and low emission. Despite these advantages, however, there are two problems with continued use of present low temperature fuel cell electrodes. The first problem is that mostly carbon supports used that suffer corrosion and the second problem is that high Pt loading needed due to low Pt utilization in the electrode. Therefore, a lot of research has been focused on new support materials that conductive polymers and oxides [1-3].

Conductive polymers have been investigated as carbon-substitute support materials for fuel cell catalysts, due to their high accessible surface area, low electrical resistance and good environmental stability. Within conductive polymers, PANI is one of the most studied materials because of its easy to synthesize in aqueous solutions, commercially available at low cost, and good redox properties and unique physico-chemical

properties. In addition, PANI has the advantage to be electron and proton conductive at the same time, and can be used as an alternative support material [4].

PANI is typically prepared by the chemical oxidation of aniline, such as aniline hydrochloride or aniline sulfate, in acidic aqueous medium. When a strong oxidant, APS, was used as the oxidant, the oligomers included oxygen and sulfur, in addition to carbon and nitrogen atoms. PANI has various oxidation states starting from leucoemeraldine (completely reduced state), emeraldine form (half oxidized) and pernigraniline (completely oxidized state). Polyaniline nanostructures like nanotubes, nanowires, nanorods and nanofibers can be prepared by various methods like rapid mixing polymerization, interfacial polymerization, in situ seeding polymerization [5-7]. Among these methods, interfacial polymerization method has achieved more attention due to its easiness, large scale production ability and environmentally benign nature. Furthermore, it has a capability to produce high quality PANI-NFs with control of their morphology, size and diameter [6].

Many studies have explored the PANI supported metal nanoparticles for catalysis and sensor applications. It has been shown that nanostructured polyanilines can significantly enhance the charge transport across the electrode/electrolyte interface and thus the electronic conductivity. But, it has been found that it is always difficult to obtain small and uniform Pt particles by the electrodeposition method. These considerations make it clear that a simple and scalable synthesis method for PANI-NFs, and a deposition method for producing small Pt nanoparticles (< 5 nm) must be developed for the application of PANI as catalyst support in PEMFCs [8, 9].

This paper aims to study the production of PANI-NFs at different aniline/oxidant ratios by an interfacial polymerization method. Pt/PANI-NFs catalysts were synthesized via the polyol method. The synthesized PANI support material and Pt/PANI catalyst are analyzed using several methods on SEM with LXRF system, XRD and FT-IR.

II. Experiment

A. Chemicals

Aniline monomer ($C_6H_5NH_2$, Aldrich, 99.9%), Ammonium peroxydisulfate ($(NH_4)_2S_2O_8$, Aldrich, >98%), Hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, China), Chloroform ($CHCl_3$, $\geq 99\%$), Hydrochloric acid (HCl, 99%), Ethylene glycol ($C_2H_6O_2$, 99%), Sodium hydroxide (NaOH, 99%), Sulfuric acid (H_2SO_4 , 65%), 18 M Ω cm de-ionized (DI) water.

B. PANI-NFs and Pt/PANI-NFs synthesis

PANI-NFs (aniline/oxidant molar ratio: (a) 4.0; b) 2.5; c) 1.0) were prepared via an interfacial polymerization method described by Stejskal and Gilbert [10]. 3 ml aniline monomer was dissolved in 200 ml chloroform and stirred with magnetic stirrer for one hour. 1.8 g ammonium peroxydisulfate was also dissolved in 200 ml hydrochloric acid (1M) and magnetically stirred for one hour. The ammonium peroxydisulfate solution was poured slowly into the aniline solution. The solution was kept at room temperature and was not stirred and not disturbed for at least 24 hours. Finally, the black green precipitate was collected by filtration (Whatman Nylon Membranes, 0.2 μm) followed by washing with 500 ml DDI water. The PANI-NFs powder was dried at ambient temperature for 24 hours.

As shown in Figure 1, Pt/PANI-NFs catalysts were prepared by an ethylene glycol (EG) reduction method. The amount of 140 mg of PANI-NFs suspended in 20 ml of EG and stirred under sonication for 10 minutes. Then, 30 ml of hexachloroplatinic acid solution kept in EG (2.0 mg Pt ml⁻¹ EG), the polymer added to solution by dropping. The solution mechanically stirred continuously for 4 hours after adding the Pt precursor. NaOH solution (2.5 M in EG) added to adjust the pH of solution to keep the balance above 12. After that the solution heated to 140°C and kept for 3 hours. Finally, solution cooled down to room temperature. 1M of aqueous H_2SO_4 used to adjust the pH balance to 2. The prepared solution then kept at 24 hours. The product filtered and washed with 1.5 l of DI water (80°C) and dried at 70°C for 8 hours. The prepared Pt/PANI-NFs catalysts have a metal loading of 14.3 wt%.

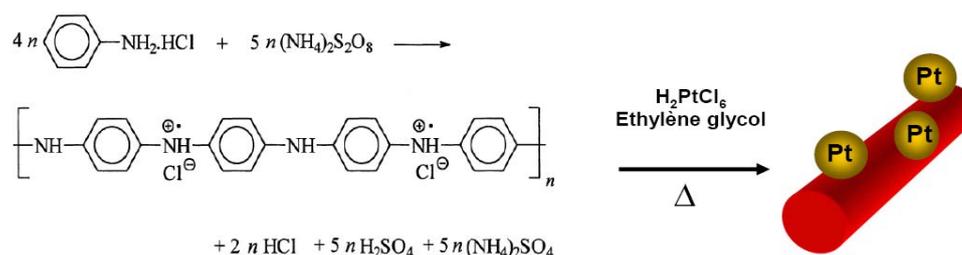


Figure 1. Schema of Pt/PANI-NFs catalysts were prepared via an ethylene glycol reduction method.

C. Characterization methods

The PANI-NFs support material and Pt/PANI-NFs catalysts were synthesized in our group and characterized using SEM, XRD and FT-IR.

For morphology and elemental analysis of all samples, SEM and EDX analysis were performed using a HITACHI SU8010 with LXRf system.

XRD analysis performed on Shimadzu XRD-7000 diffractometer using monochromized $\text{CuK}\alpha$ ($\lambda=1.5418 \text{ \AA}$) radiation at room temperature. Measured diffraction patterns refined by Rietveld method using software package WinPLOTR [11].

FT-IR measurements were collected on a Thermo Nicolet iS10 with MCT/A detector, in region of $4000 - 650 \text{ cm}^{-1}$ by KBr pellets.

III. Results and discussion

Figure 2 shows the SEM images of the synthesized PANI-NFs by interfacial polymerization method with 4; 2.5; 1 aniline/oxidant molar ratios and Pt/PANI-NFs catalyst. From SEM results in Figure 2 (a – d), it is clearly shown that by decreasing the molar ratio from 4 to 1, the PANI-NFs tend to agglomerate and form micro size particles. As seen in Figure 2a when the aniline/oxidant molar ratio is 4.0, the more uniform nanofibers with a mean diameter 50 nm have been produced. By decreasing the molar ratio to 2.5 (Figure 2b), almost uniform PANI-NFs are produced with an average diameter of 60 nm. When the molar ratio reached to 1 (Figure 2c), the polyaniline with high level agglomeration is formed and low amount of nanofibers were produced. These results, we concluded that an important factor which might influence on the morphology of the PANI-NFs is the aniline/oxidant molar ratio. Figure 2d shows the morphology of the Pt/PANI-NFs catalysts and from SEM results, it is clearly seen that Pt nanoparticles (about 2 nm) are uniformly distributed on the surface of PANI-NFs.

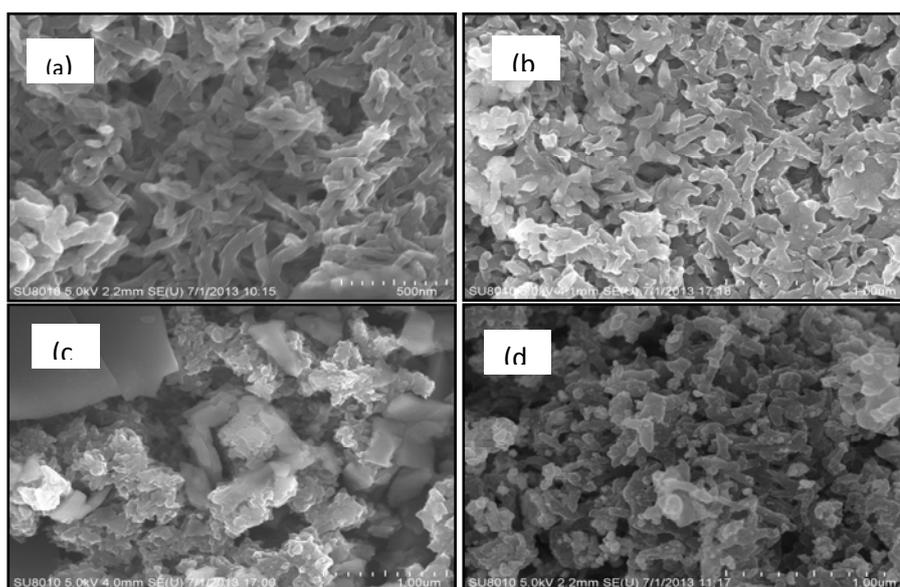


Figure 3 shows SEM image of PANI-NFs, Pt/PANI-NFs samples and their EDX spectra. As shown in Figure 3 (a, b) the synthesized PANI has nanofiber (~50-70 nm) morphology and Pt particles were uniformly dispersed on the PANI surface. Figure 3 (b, d) shows the results of the EDX analysis of the content elements of catalysts. In particular, we observed the presence of C(~80%), N(~11%), O(~7%) and Cl(~2%) in the PANI-NFs supports (Figure 3b). The EDX spectrum shown in Figure 3d revealed Pt(~8%), C(~70%), N(~12%), O(~9%) and Cl(~1%) in the Pt/PANI-NFs catalysts.

Figure 4 shows XRD patterns of PANI-NFs with different aniline/oxidant molar ratios (PANI-4.0, PANI-2.5, PANI-1.0) and Pt/PANI-NFs with Rietveld refinement. XRD analysis indicates the crystallinity of the product. High crystalline products could display metallic behavior and they are more useful than amorphous products. Generally, percent of the polymer crystallinity (X_C) can be calculated from this ratio [12]:

$$X_C = \frac{A_C}{A_A + A_C} \cdot 100\%, \quad (1)$$

where A_C – Area of crystalline phase, A_A – Area of amorphous phase.

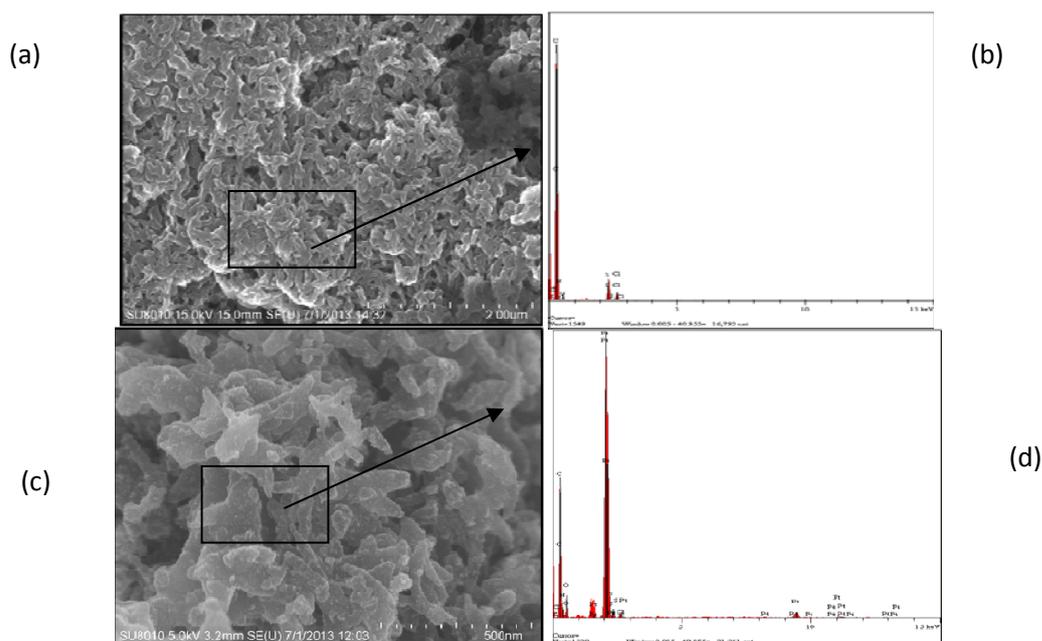


Figure 3. SEM images of PANI-NFs, Pt/PANI-NFs samples and their EDX spectrum.

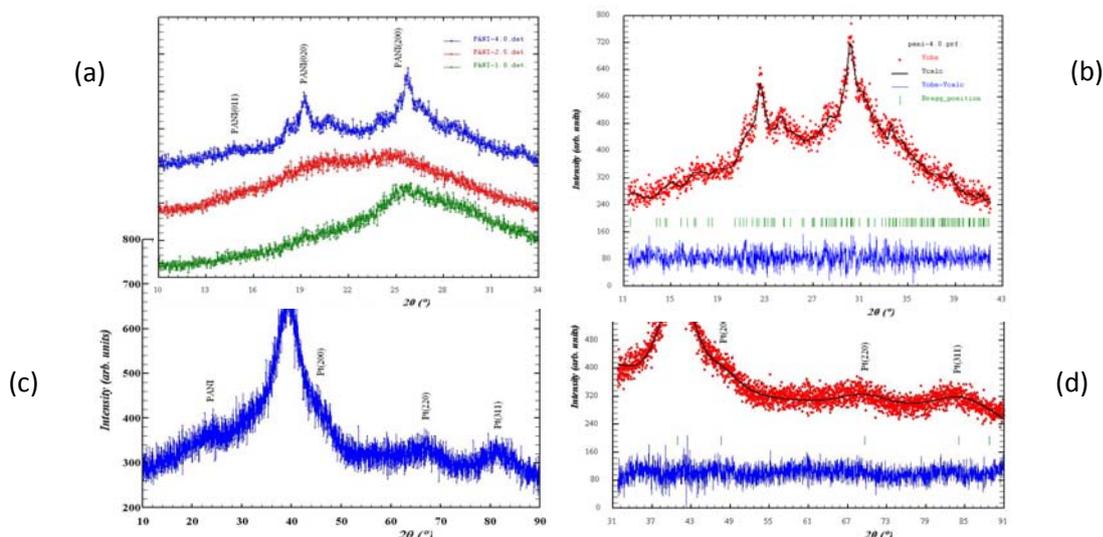


Figure 4. XRD patterns of (a, c) PANI-NFs with different aniline/oxidant molar ratios (PANI-4.0, PANI-2.5, PANI-1.0) and Pt/PANI-NFs, (b, d) with Rietveld refinement of Pt/PANI, PANI-NFs

Rahy et al. [12] shows that the crystalline PANI has an X ray diffraction pattern consisting of three peaks at 15° , 20° and 25° . As shown in Figure 4a (PANI-4.0 – blue line) three sharp peaks appeared at $2\theta=14.8^\circ$, 19.2° , 25.7° , reveal that PANI-NFs with aniline/oxidant = 4 has crystalline properties. The characteristic peaks appeared at 14.8° , 19.2° and 25.7° , corresponding to (011), (020) and (200) crystal planes of PANI. As shown in Figure 4a (PANI-2.5 – red line) the broad peaks of amorphous phases appeared at $2\theta = 20.5^\circ$, 25.6° , corresponding to (020), (200) crystal planes. Also, Figure 4a (PANI-1.0 – green line) shows that the broad peaks at $2\theta = 25.7^\circ$ reveal that PANI with aniline/oxidant = 1 is in the amorphous state. On the other hand, the percent crystallinity of PANI-4.0, PANI-2.5 and PANI-1.0 as calculated by using Eq.1 are $\sim 41\%$, $\sim 24\%$ and $\sim 14\%$, respectively.

The diffraction peaks observed at $2\theta < 35^\circ$ are attributed to the PANI supports. The diffraction peaks at $2\theta > 35^\circ$ show that Pt nanoparticles are present in the face-centered cubic (fcc) structure, as indicated by characteristic peaks of (111), (200), (220) and (311). The average crystallite sizes of Pt and PANI particles for Pt/PANI-NFs catalysts were calculated using Scherrer equation (Eq.2), considering the full-width at half maximum (FWHM) and angle of the position of the maximum (θ), obtained at Gaussian fit of (220) reflection.

$$D = \frac{k\lambda}{FWHM \cdot \cos\theta}, \quad (2)$$

where k is Scherrer coefficient (0.9), λ is the wave length of x-ray.

The crystallite size (D), Rietveld refinement R_p and R_{wp} values for PANI-4 and Pt/PANI-NFs samples are given in Table 1.

Table.1 Rietveld refinement

Samples	Crystallite size (Å)	R_{wp} factor (%)	R_p factor (%)
PANI-4	30	5.66	4.47
Pt/PANI-NFs	11	5.42	4.27

Figure 5 shows FTIR spectra of PANI-4, PANI-2.5, PANI-1 support materials and Pt/PANI-NFs catalyst. As shown in the spectra of all samples, the peaks are approximately presented at 3434cm^{-1} , 1567cm^{-1} , 1491cm^{-1} , 1300cm^{-1} , 1129cm^{-1} , at 810cm^{-1} . In a spectrum the peak observed at 3434cm^{-1} is due to N-H stretching vibration. The main peaks at 1567cm^{-1} and 1491cm^{-1} can be associated with C=N and C=C stretching vibrations of quinoid and benzene rings, respectively. The peaks at 1300cm^{-1} and 1249cm^{-1} are attributed to the C-N stretching mode. The peak at 1129cm^{-1} is due to quinonoid unit of doped PANI. The peak at 810cm^{-1} , 790cm^{-1} , 874cm^{-1} and 823cm^{-1} is attributed to the out-of-plane bending of C-H of all samples. These related peaks confirm the successfully formation of PANI at different aniline/oxidant molar ratios by interfacial polymerization method.

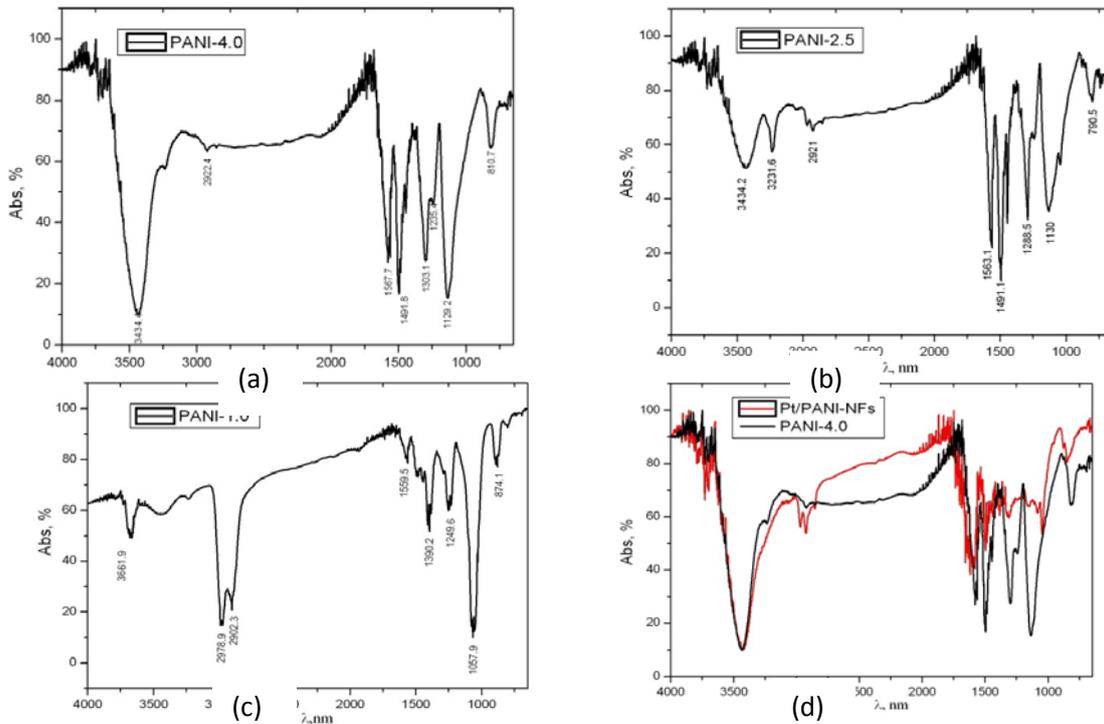


Figure 5. FT-IR spectra of (a) PANI-4, (b) PANI-2.5, (c) PANI-1 support materials and (d) Pt/PANI-NFs catalyst

IV. Conclusion

The PANI and Pt/PANI-NFs were successfully prepared chemically by an interfacial polymerization and ethylene glycol reduction method, respectively. It has been found that different aniline/oxidant molar ratios affected the uniformity and morphology of polyaniline. As shown in SEM analysis the synthesized polyaniline has nanofiber (~50-70 nm) morphology and Pt particles were uniformly dispersed on the PANI surface. The more uniform and thinner polyaniline nanofibers have been achieved at aniline/oxidant molar ratios = 4. XRD results show that PANI-NFs with more uniformity at aniline/oxidant molar ratios = 4 has higher crystallinity rather than irregular shaped polyaniline. We were calculated percent crystallinity for PANI-4.0, PANI-2.5 and PANI-1.0 as ~41%, ~24% and ~14% from XRD analysis. Also, the average crystallite sizes of Pt and PANI for Pt/PANI catalyst determined from XRD data as 11Å , 30Å . FT-IR results also show that the PANI products have similar molecular structure in different aniline/oxidant molar ratios. Our study concluded, that Pt/PANI-NFs is a very promising candidate for cathode catalyst of PEMFC.

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X-Ray Absorption Study of Magnetic Powder Materials (La_xCe_{1-x})MnO₃ AND (Mg_xCu_{1-x})Fe₂O₄

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Abstract

Perovskite type oxides with general formula ABO₃ may potentially replace noble metal catalysts due to their high activity, thermal stability and low costs [1]. The catalytic properties of ABO₃ basically depends on the nature of A and B ions. Therefore the electronic properties and catalytic activity of the perovskite-type oxides can be modified by substitution of other heterovalent ions into the A or B sites [2].

Cerium doped lanthanum cobaltite perovskites (La_{1-x}Ce_xCoO₃ with x=0, 0.2, 0.4) were prepared by the sol-gel method and characterized by X-ray diffraction (XRD), X-ray absorption (XAS), Energy dispersive X-ray spectroscopy (EDS). The results showed that the cerium doping promoted the structural transformation of LaCoO₃ from rhombohedral into cubic structure. High specific surface area and small crystallite size are achieved with x=0.2. The XAS results confirmed the formation of compound La_{1-x}Ce_xCoO₃. The structural parameters were determined by Rietveld analysis of the diffraction profiles. XAS measurements for Ce L₃, La L₃ and Co K- edges recorded at beam lines BL17C1 of National Synchrotron Center, Hsinchu, Taiwan. The data fitting was performed using the software package IFEFFIT.

Keywords powder materials, X-ray diffraction, IFEFFIT.

Синхротронное абсорбционное исследование магнитных порошковых материалов (La_xCe_{1-x})MnO₃ и (Mg_xCu_{1-x})Fe₂O₄

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Аннотация

Оксиды типа перовскита с общей формулой ABO₃ потенциально могут заменить катализаторы из благородных металлов благодаря их высокой активности, термической стабильности и низкой стоимости. В этой работе изучены структурные свойства ABO₃, связанные с особенностью взаимного расположения ионов гетеровалентных в узлах А и В.

Церия кобальтит, легированный лантаном (La_{1-x}Ce_xCoO₃ с x = 0, 0,2, 0,4) и медный феррит со структурой шпинели, легированный магнием (Mg_xCu_{1-x})Fe₂O₄ были исследованы методом поглощения синхротронных рентгеновских лучей (XAS). Измерения XAS для (La_{1-x}Ce_xCoO₃) выполнено на пучке BL17C1 Национального синхротронного центра, Синьчжу, Тайвань, а эксперименты XAS по (Mg_xCu_{1-x})Fe₂O₄ проводились на пучке 1W1B рентгеновского поглощения тонкой структуры в синхротронном центре Пекинского электрон-позитронного коллайдера (BEPC) в Китае. Обработка экспериментальных данных проводилась на пакетной программе IFEFFIT.

Ключевые слова: порошковые материалы, рентгеновские лучи, IFEFFIT