

## Preparation and characterization of La-Co alloy nanowire arrays by electrodeposition in AAO template under nonaqueous system

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**Abstract:** La-Co alloy nanowires can be made in pulse reversal current (PRC) and direct current (DC) electrodepositions under nonaqueous system, with the porous anodic aluminum oxide (AAO) as template. This membrane is subject to the dual-oxidation (two-step) anodizing. Scanning electron microscope (SEM) examination shows that all of the nanowires have uniform diameter about 200 nm, and their diameters are determined by the pore diameter of applied AAO template. X-ray energy dispersion analysis indicates that the chemical composition of La and Co elements is very close to 1:2 in stoichiometry. X-ray diffraction pattern investigation demonstrates that La-Co nanowire is the face-centered cubic (FCC)  $\text{LaCo}_{13}$ .

**Key words:** La-Co alloy; nanowire arrays; electrodeposition; AAO template

### 1 Introduction

Recently, nanosized materials, such as nanoparticle, nanowire and nanoarray have received much attention due to their extraordinary electronic[1], optical[2] and chemical[3] properties. In order to obtain nanostructure, several technologies, such as lithographic method and the bottom up approach, have been developed to promote the progress. The anodic aluminum oxide (AAO) template medium technique is currently employed to fabricate the regular and aligned nanoarrays[4–5]. The template synthesis for metal nanowires, pioneered by MARTIN et al[6], MOSKOVITS et al[7] and SEARSON et al[8], involves the deposition of metal into the cylindrical pores of an inert, nonconductive host material (such as porous  $\text{Al}_2\text{O}_3$  films). In addition, the electrochemical deposition (ECD) is regarded as an inexpensive and easy method to synthesize material. The combination of AAO template and ECD is an efficient method to fabricate nanoarrays of metals[9]. Being conventionally functional materials, rare-earth (RE) compounds (hydroxides, oxides, rare earth alloy, etc.) have been widely used in various fields in the past

decades, including high-performance luminescent devices, magnets and catalysts[10–11]. Lanthanum, one of the rare earth (RE) elements, has been applied successfully in many fields, such as metallurgy[12] and chemical engineering[13–14]. So far, many researches have been conducted or under way[15–19]. However, there is few published works about the template-electrodeposition preparation of La-Co alloy nanowire arrays in nonaqueous system. Metal compounds transferred from RE, such as  $\text{LaCo}_5$ ,  $\text{SmCo}_5$ ,  $\text{Sm}_2\text{Co}_{17}$  and  $\text{Nd}_2\text{Fe}_{14}\text{B}$ , dominate the field of permanent magnets, which includes the high coercive fields  $iH_c$  and/or maximum energy product  $(BH)_{\max}$ . Development of RE permanent magnet market will be described in this work.

Porous AAO template is a widely studied material, which is used for the fabrication of one-dimensional nanometer-scale structure as a medium template in recent years. The reason is that its morphology exhibits a lot of homogeneous parallel pores growing perpendicular to surface with a narrow distribution of diameter from 10 to 400 nm and its depth can be well controlled from several nanometers to several micrometers. It also exhibits good chemical inertia and fine physical stability. As a result, by combining its properties with the electrochemistry,

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vacuum, electroplating and chemical aggregation synthesized technology, the template can be widely applied in controllably ordered growth and assembling techniques of various nanowires and nanotubes[20].

In this work, the new method was adopted, i.e. the growth of La-Co alloy nanowire arrays in AAO template was introduced in means of template-electrodeposition under carbamide-NaBr-KBr-formamide of low-temperature molten salt system. The structure and morphology of the nanowires were characterized and discussed based on the initial research on the magnetic performance of La-Co alloy nanowires.

## 2 Experimental

### 2.1 Preparation of AAO template

The high purity aluminum (99.999%) plate was cut into pieces of 1 cm×2 cm. The aluminum pieces were subject to special treatment. A mirror surface was achieved by electropolishing in the solution with H<sub>2</sub>ClO<sub>4</sub> to alcohol ethylic volume ratio in 1:3 at room temperature[21].

Two-step anodizing method was used to produce an ordered porous aluminum oxide layer on the surface of the aluminum plate. The interval between anodic alumina porous, or called as the cell size, was controlled by the voltage supplied for anodization. In this experiment, a 35 V DC voltage was applied between the AAO template working electrode and graphite counter electrode in 0.3 mol/L H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> aqueous solution for 1 h at room temperature. The precursor template was then rinsed in distilled water and the oxide layer were dissolved in the mixed acid of 6% H<sub>3</sub>PO<sub>4</sub> (mass fraction) and 1.5% CrO<sub>3</sub> (mass fraction) for 1 h at room temperature.

The second anodizing step was performed in the same experimental condition as the first step (temperature, electrolyte concentration and anodizing voltage). The template membrane was separated from the Al substrate by immersing the treated sheet in saturated HgCl<sub>2</sub> solution. The membrane was rinsed with distilled water and then immersed in 5% H<sub>3</sub>PO<sub>4</sub> solution for about 30 min at 30 °C to dissolve the barrier-type part on the bottom of nanoholes. The hole in AAO template was

about 200 nm in diameter and 10 μm in depth after this treatment. Finally, a platinum film was deposited by vacuum evaporation onto one surface of the AAO template so as to provide a conductive contact.

### 2.2 Preparation of La-Co alloy nanowire arrays

The La-Co alloy nanowire arrays were fabricated through electrodeposition using AAO template of PRC and DC[22]. The electrolyte and electrodeposition parameters are listed in Table 1. A graphite rod was used as the counter electrode and the Pt/AAO.

Template was used as working electrode. The electrodeposition was normally conducted for 30 min for the La-Co alloy nanowire growth, and then the deposited specimen was cleaned with deionized water to remove the remaining contaminants. Finally, the free-standing La-Co alloy nanowire arrays were obtained by removing the AAO template with NaOH solution.

### 2.3 Characterization of La-Co alloy nanowire arrays

The phases of La-Co alloy nanowire were identified by the X-ray diffractometry (XRD, X'PERT PRO) using Cu K<sub>α</sub> radiation. The morphology of the AAO templates and La-Co alloy nanowire arrays was observed by scanning electron microscopy (SEM, JEOL JSM-5910LV). The chemical composition of the nanowires was determined with energy dispersive X-ray spectrometer (EDS, Oxford Instruments 7274).

## 3 Results and discussion

### 3.1 Mechanism of two-step anodizing method with AAO template

In the process of aluminum anodizing, the formation of the oxidized-alumina porous membrane on the metal aluminum is the interactive result by the chemical dissolution and the electrochemical dissolution under the function of electric field, and it is a complicated process involving physical, chemical, electrochemical and other disciplines. The said two-step refers to the oxidization for two times. Firstly, the aluminum plates are subject to oxidization under certain conditions for a certain period and the alumina membrane

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**Table 1** Electrolyte and electrodeposition parameters

$\rho(\text{Urea})/(\text{g}\cdot\text{mL}^{-1})$	$\rho(\text{NaBr})/(\text{g}\cdot\text{mL}^{-1})$	$\rho(\text{KBr})/(\text{g}\cdot\text{mL}^{-1})$	$V(\text{formamide})/\text{mL}$	pH	Temperature	Stirring speed/ ( $\text{r}\cdot\text{min}^{-1}$ )		
0.474	0.20	0.018	100	2	Room temperature	250		
PRC					DC			
$J_{a,p}/(\text{A}\cdot\text{m}^{-2})$	$r_p$	$(t_{p,on}+t_{p,off})/\text{ms}$	$J_{a,r}/(\text{A}\cdot\text{m}^{-2})$	$r_r$	$(t_{p,on}+t_{p,off})/\text{ms}$	Total plating time/ min	Current density/ $(\text{A}\cdot\text{m}^{-2})$	Total plating time/min
200	0.3	3	20	0.1	3	30	1 500	30

$J_{a,p}$ ,  $J_{a,r}$ —Average current densities of positive and reverse pulse, respectively;  $r_p$ ,  $r_r$ —Positive pulse duty cycle and reverse pulse duty cycle, respectively;  $t_{p,on}$ ,  $t_{p,off}$ —Positive and reverse pulse on-time, respectively;  $t_{p,off}$ ,  $t_{r,off}$ —Positive and reverse pulse off-time, respectively.

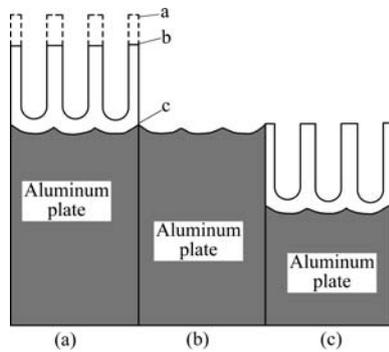


Fig.1 Process of two-step anodizing oxidation

is obtained, as shown in Fig.1(a). From the self-organized mode, if oxidation duration is longer, the nanoholes will be arrayed more regularly. This is because the growth of nanoholes is interacted by the vertical electrical-field force of outside electric field and the horizontal electric-field force repelling each other among the  $\text{HC}_2\text{O}_4^-$  groups in the electrolyte, and consequently is in the disorder state. If oxidation time is long enough, together with the rise of temperature and increasing the thermal movement of  $\text{HC}_2\text{O}_4^-$  and other factors,  $\text{HC}_2\text{O}_4^-$  in the nanoholes is inclined for even distribution, which, actually, can weaken the orientation of horizontal electric field and enable the growth of nanoholes from disorder to order state. Near to the barrier layer ("c" in Fig.1), the nanoholes will be arrayed more regularly. In the aluminum anodizing process, if the vertical growth rate of nanoholes is converging to the dissolving rate of AAO membrane in electrolyte, the thickness of porous layer will become unvaried. If the oxidation is stopped, and the alumina membrane is eliminated by the dissolution in released liquid or by reverse-stripping method[23], the entire AAO membrane will make level shift to the aluminum base body. We can have the aluminum, as shown Fig.1(b). The orderly nano-traces at the plane of barrier layer "c" can be kept completely[24]. At Last, the oxidation for second time will be conducted under identical conditions. The nanoholes will continue growing alongside the original sequences and traces and the orderly nanohole arrays will be acquired. Obviously, if the duration for the first-time oxidation is longer, the nanohole array obtained by means of dual-oxidation will be more orderly.

Fig.2 shows the SEM images of the as-anodized and prolonged AAO templates. The diameter of the pores in the as-anodized template is about 50 nm, and is enlarged to about 200 nm for 30 min. As the time prolongs, the diameter of the pores increases, but the distance between

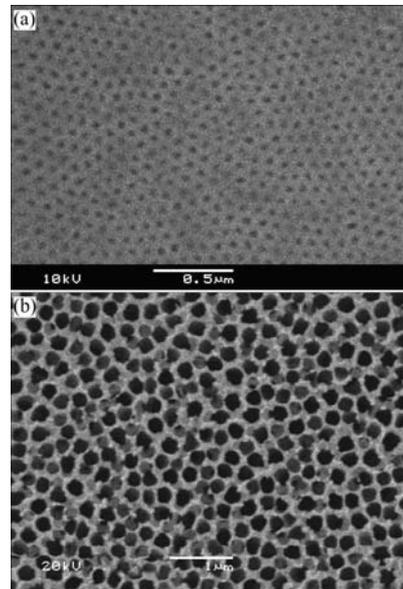


Fig.2 SEM images of AAO templates with inter-pore distance of 200 nm: (a) As-anodized; (b) Anodized for 30 min

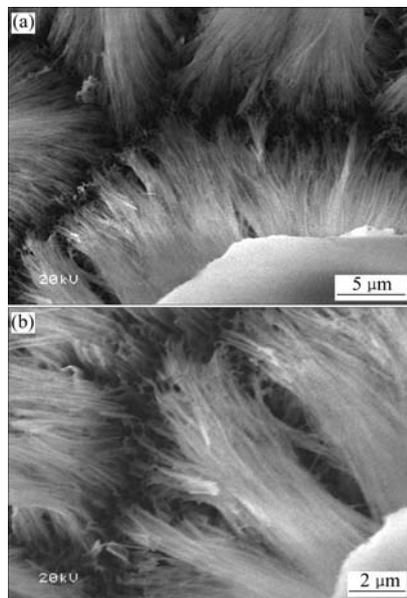
the pore centers does not change, i.e. about 200 nm.

### 3.2 Surface morphology and microstructure

Fig.3 shows the surface and cross-section morphologies of the DC and PRC La-Co alloy nanowire. It is found that, compared with the DC La-Co alloy nanowire (Fig.3(a)), the PRC La-Co alloy nanowire (Fig.3(b)) appears finer and compacter.

Fig.3 shows the typical SEM image of La-Co alloy nanowires prepared by electrodeposition in AAO template with pore diameter of about 200 nm. It can be seen that the average diameter of the nanowires is about 200 nm, which closely corresponds to the diameter of the pores in the used AAO. It can also be seen from Fig.3 that the length of the uniform nanowires is about 10  $\mu\text{m}$ , and the quantity of the nanowires is very huge.

The results of the present experiment show that the means of PRC could give fine and long nanowires. The results may be attributed to increased electrochemical polarization of cathode during the on-time of pulse current period, which decreases the nucleation energy of the metal deposition on the electrode surface and increases nucleation rate. As a consequence of the high nucleation, it leads to the increase of the number of nucleation centre. In addition, in the process of PRC, the alternative of positive current and reversal current can make the surface state of electrodes change, such as



**Fig.3** Surface and cross-section morphologies of La-Co alloy nanowires (SEM): (a) DC La-Co alloy nanowires; (b) PRC La-Co alloy nanowires

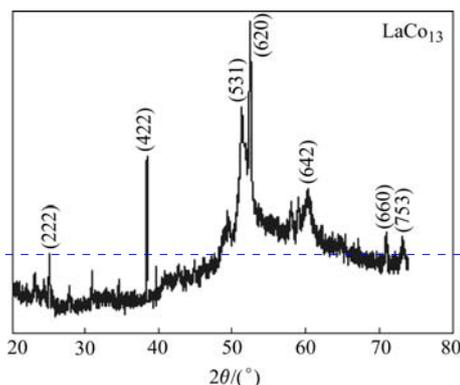
adsorption phenomena, surface diffusion layer structure and electrical double layer structure, which results in the clearing and activation of the metallic surface in turn and is favorable to improve the purity of the composite[25–26]. Consequently, the texture of PRC nanowires possesses fine length and compact microstructure.

The principle that RE raises the electrodeposition rate of metal[27] can well explain the fact that the La-Co alloy is more inclined to form and more compacted once the RE La is added. To those RE elements (La, Ce, etc.) that lie at the Third Deputy Communities in Periodic Table, as their 4f electron does not tightly enclose the atomic nucleus and their screening factor is less than that of the other electrons with same principal quantum number, the effective nuclear charge number is large and strong adsorption capacity is demonstrated. When an appropriate amount of them are added into the plating liquid, firstly, they can make preferential adsorption defects on the surface of base body, thus lowering the substrate surface energy, improving the nucleation rate and accelerating the deposition; secondly, the RE, if it appears in the form of positive ions, can act as a catalyst to accelerate the decomposition of main salt  $\text{CoCl}_2$  and the reduction of  $\text{Co}^{2+}$ ; thirdly, the RE and some transition metal ions can reduce mutual activity and increase solubility each other, thus, it can carry with the deductive

deposition of fundamental metal ions on the surface of base body; fourthly, the RE ions can also form complex with other organic or inorganic coordinating substance, consume some of the complex bases of complexant, and enlarge the concentration of main salt's metal ions dissociative in the plating liquid, hence increase the electric potential difference of interface, promote the transition of active particles to the surface of base body and speed up the sedimentation rate.

### 3.3 XRD analysis

The X-ray diffraction pattern for the sample is shown in Fig.4. The diffraction peaks at  $2\theta=27.334^\circ$ ,  $38.957^\circ$ ,  $47.568^\circ$ ,  $50.915^\circ$ ,  $61.164^\circ$ ,  $70.417^\circ$  and  $76.515^\circ$  correspond to the (222), (422), (531), (620), (642), (660) and (753) diffraction peaks of face centered lattice- $\text{LaCo}_{13}$  crystalline, respectively.



**Fig.4** XRD pattern for sample consisting of La-Co alloy nanowires and AAO template

### 3.4 Energy disperse spectroscopy(EDS) analysis

The chemical composition of the La-Co alloy nanowires is determined by energy dispersive X-ray spectrometer(EDS). The EDS spectrum, shown in Fig.5, reveals that the nanowires contain Co and La. Quantitative analysis results, given in Table 2, indicate that the composition of the nanowires is 21.63% La and 50.78% Co, which is very close to 1:2 of molar ratio. As the samples used in the EDS analysis can not be applied with vinyl alcohol protection film and the installation of samples must be done in the air, the surface of samples is oxidized partially (below 3.5%), while a few of aluminum (0.06%) residual is caused by the AAO template.

### 3.5 Magnetic property of La-Co alloy nanowires

The magnetism of La-Co alloy nanowires are obtained from hysteresis loops measured with the

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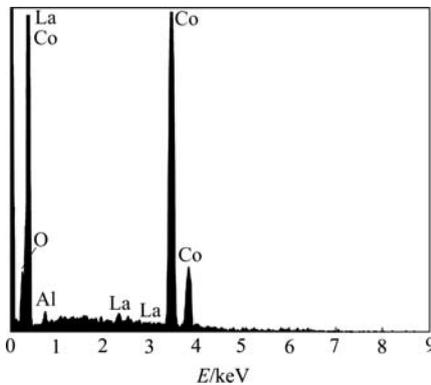


Fig.5 EDS spectrum of La-Co alloy nanowires prepared by template electrodeposition in AAO

Table 2 Component of AAO template deposited La-Co alloy

Element	Mass fraction/%	Molar fraction/%
O	3.39	12.46
Al	0.06	0.13
Co	80.90	80.78
La	15.65	6.63
Total	100.00	

magnetic field parallel to the wire axis. The testing conditions are as follows: sample sensitivity 2 mV, corresponding voltage 5 410 mV; sample sensitivity 500  $\mu$ V, corresponding voltage 101.796 mV; at room temperature (as shown in Fig.6). The perfect symmetrical loop is displayed. The saturated magnetization intensity ( $M_s$ ), coercive force ( $H_c$ ) and the maximum energy product  $(BH)_{\max}$  are 129.63  $\text{Am}^2/\text{kg}$ , 0.010 8 T and 865  $\text{J}/\text{m}^3$ , respectively. This kind of rare earth alloy nanowire prepared from low temperature melting salt bath could be expected in same application as magnetic materials.

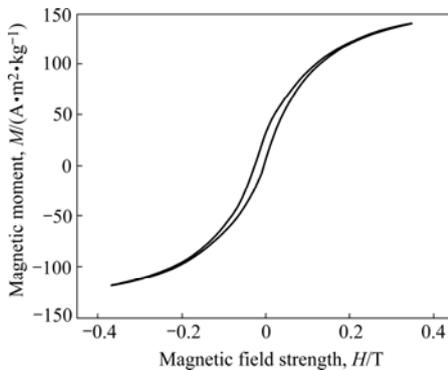


Fig.6 La-Co alloy settled layer hysteresis loop

## 4 Conclusions

1) We have successfully prepared the ordered and free-standing La-Co alloy nanowire arrays by electrodeposition method in the solution of urea-NaBr-KBr-formamide system using AAO templates.

2) The composition and crystal structure of nanowires can be controlled by pulse reversal electrodeposition (PRC) and direct current electrodeposition (DC). SEM and XRD results indicate that the diameter and length of the electrodeposited La-Co alloy nanowires are closed to those of the pores in used AAO template, around 200 nm. The obtained La-Co alloy nanowires are of face-centered lattice  $\text{LaCo}_{13}$  crystalline.

3) Both qualitative and quantitative EDS analysis have been made on the samples and the findings tell us that the sample contains 21.63% La and 50.78% Co (molar fraction), and the mole ratio between two elements is nearly 1:2.

4) The hysteresis loop of La-Co alloy can tell us that the saturation reaches when the field strength is 0.35 T, the saturated magnetic moment is 129.63  $\text{Am}^2/\text{kg}$ , the maximum energy product  $(BH)_{\max}$  is 865  $\text{J}/\text{m}^3$  and the coercive force is 0.010 8 T.

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