



Synthesis and electrochemical study of La-doped RuO₂–TiO₂/Ti coatings

XIAOYU JIANG^{1*}, SHUAI LI¹, ZHIGANG ZHANG¹, HANG XIAO¹, WEIQIN WU¹,
LANG LIN¹, XIAOYUAN WU², WEI LI³, LEI ZHANG³ and WENZHE CHEN³

¹College of Ecological Environment and Urban Construction, Fujian University of Technology, Fuzhou, P. R. China, ²State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, P. R. China and ³College of Material Science and Engineering, Fujian University of Technology, Fuzhou, P. R. China

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Abstract: La-doped RuO₂–TiO₂/Ti coating (TRL) and RuO₂–TiO₂/Ti coating (TR) were prepared by the sol–gel method and thermal treatment. The products were characterized by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). The electrochemical properties were investigated by cyclic voltammetry and polarization measurements in O₂ and Cl₂ evolution in H₂SO₄ and NaCl solution. The XRD analysis showed that in both TRL and TR, the particles of the synthesized coatings were of low crystallinity, and that they were mainly formed of two phases, rutile TiO₂ and RuO₂. SEM confirmed that the surface of TRL and TR coatings had a cracked mud appearance consisting of blocks separated by cracks. The morphology of the TRL coating shows irregular crack blocks, which increased the specific area greatly and provides more active sites. Polarization measurements indicate that the onset potential of chlorine evolution reaction for TRL coating was 1.08 V_{SCE}, which is lower than the value of 1.12 V_{SCE} registered for the TR coating. The onset potentials for oxygen evolution for the two coatings were similar. Cyclic voltammetry shows an improvement of the electrochemical capacity for the La-doped coatings.

Keywords: La-doped RuO₂–TiO₂/Ti coating; synthesis; thermal decomposition; cyclic voltammetry (CV); polarization measurements.

INTRODUCTION

Metallic-oxide electrodes have been widely studied because of their electronic, optical, magnetic and catalytic properties.^{1–4} Electrodes consisting of a titanium substrate covered with an oxide coating are applied as the anode (commonly known as dimensionally stable anode, DSA) in a number of important

* Corresponding author. E-mail: xyjiang@fjut.edu.cn
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electrolytic processes, such as oxygen or chlorine evolution, the electrochemical oxidation or degradation of organic pollutants in wastewaters, *etc.*^{4–6}

Electrochemical activity and chemical stability, crucial for an anode material, are mainly related to the chemical composition and the structure of the coating. Many researches have focused on designing new ways and adding various chemical compositions to improve the electro-catalytic activity and chemical stability. Some types of metal oxide electrodes, such as SnO₂, PbO₂, Sb₂O₃, RuO₂ and composite oxides, have been widely studied,^{7–11} and the higher reaction activity is expected all the time.

RuO₂-based material exhibits low resistivity, high thermal stability and high resistance to chemical corrosion¹ and has become research focus recently.^{5,12–14} It is suggested that the enhancement of the electrode for electrochemical oxidation of organics could be attributed to the production of hydroxyl radicals.^{15,16} In electrochemical processes, the doping of rare earth and other metals into the film could improve the surface structure and enhance the electrode capability on mineralization of pollutant compounds.^{4,16–18}

In this study, La was selected as co-dopant to introduce into RuO₂-TiO₂/Ti coating by thermal decomposition. The effect of the La oxide on the electro-catalytic activity has been studied from polarization and cyclic voltammetry measurements.

EXPERIMENTAL

Coating preparation

All chemicals and solvents were commercially available and used without further purification. Commercial pure titanium foils (grade 2, size 100 mm×160 mm) were used as substrate, which were cleaned with a concentrated sulfuric acid (H₂SO₄) solution prior to sol-gel process. Tetrabutyl orthotitanate (TBOT) and ruthenium chloride (RuCl₃·3H₂O) were used as starting materials for sol-gel process. TBOT (1.0 g) was dissolved in a mixture of 10 ml ethyl alcohol and 0.1 ml hydrochloric acid, keeping the system under constant stirring for 6 h and a clear TiO₂ sol was formed. The RuO₂ sol was prepared by the addition of solid RuCl₃·3H₂O (0.35 g) to stirred mixture of ethyl alcohol (5 mL) and 2-propanol (5 mL), and the stirring was continued for 2 h. La oxide nanoparticles are prepared as describe in the literature.¹⁹ Thus, La(NO₃)₃·6H₂O (4.3g) was added to stirring aqueous solution of citric acid (30 mL, 0.5 mol L⁻¹) and ammonia was added to adjust pH 9, kept stirring for 2 h and roasted at 600 °C for 2 h after standing for one week. The all obtained TiO₂ and RuO₂ sols were mixed under stirring at ambient temperature, and La oxide (according to stoichiometric ratio) was added and kept stirring for 6 h. Then, the precursor sol was ready for running the painting process.

A layer of the precursor sol was applied by painting. Afterward, the coating was dried at 100 °C in an oven for 10 min and then roasted at 450 °C for 10 min. The painting, drying and roasting were repeated and the final coating was annealed at 500 °C for 2 h. The calcination process was aimed at the elimination of all the organic materials and the formation of metallic oxides. In addition to the La-doped RuO₂-TiO₂/Ti coating (TRL), a RuO₂-TiO₂/Ti coating (TR) was prepared as a comparison. The calculated mole ratios of Ti:Ru:La were 7:3:0.5 for TRL and 7:3:0 for TR.

Physical characterization and electrochemical measurements

The surface morphologies of the coatings were observed by means of a field emission scanning electron microscope (FESEM, S-4160). X-Ray diffraction (XRD) analysis was performed with CuK_α radiation, using a Rigaku miniflex instrument for the powder samples and a Bruker D8 Advance instrument for the coatings. Electrochemical measurements were performed on a CHI 760 electrochemical workstation with a three-electrode system. A platinum electrode was used as the counter and a saturated calomel (SCE) electrode as the reference. The electrochemical behavior of the coatings was studied using polarization and cyclic voltammetry tests in: 1) 0.5 mol L⁻¹ NaCl, 2) 1.0 mol L⁻¹ H₂SO₄ and 3) 0.5 mol L⁻¹ NaCl + 1.0 mol L⁻¹ H₂SO₄ solutions purged with nitrogen at ambient temperature at a scanning rate of 100 mV s⁻¹ without *IR* compensation.

RESULTS AND DISCUSSION

Characteristics of the coatings

The surface morphology of coatings on titanium substrate is shown in Fig. 1. The microstructure of both coatings was similar to cracked mud consisting of blocks separated by cracks. The cracked blocks border zone appeared brighter than the bulk of the islands, which is usually assigned to edge segregation of titanium oxide.²⁰ The cracked blocks were smaller and rougher in the TRL coating compared with those in the TR coating. The results indicate a larger surface area and a less uniform composition in the La-doped coating TRL than in the TR coating. The energy dispersive X-ray spectroscopy (EDS) analysis indicated the element La in the TRL coatings. The mole ratios of Ti:Ru:La were 7:2:0.4 in the TRL coating surface and 7:2.1:0 in the TR coating surface, where the amount of Ru was a little lower than the calculated value.

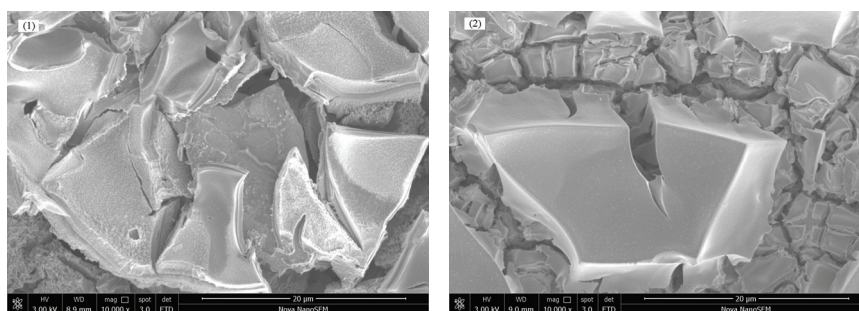


Fig. 1. Scanning electron micrographs for TRL (1) and TR (2) coatings on titanium.

The results of X-ray diffraction spectrum for the coatings and powder samples are shown in Fig. 2. It appears that the low crystallinity of the synthesized particles was maintained in the coatings. Both the TRL and TR coatings contained the phases rutile TiO₂ and RuO₂, which is consistent with typical TiO₂/RuO₂ coating.^{12,21–24} The presence of metallic Ti peaks in the TRL and TR coatings arise from the Ti substrate. The powder samples were formed

mainly of the phases rutile TiO_2 and RuO_2 . There might be two reasons for no obvious new phase of La oxide in the XRD spectroscopy. One is the small amount of La in comparison to the rutile TiO_2 and RuO_2 phases, and the other is that La may occupy metal site in the rutile phases.²⁵

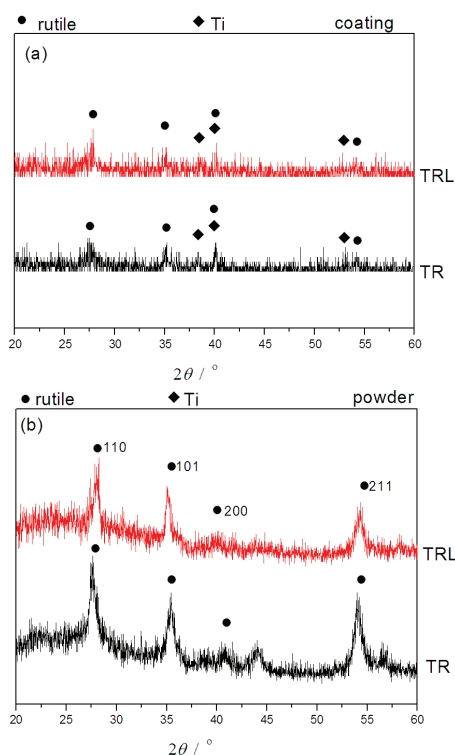


Fig. 2. XR diffraction spectrum for: a) the coatings and b) powder samples.

Electrochemical measurements

The oxygen evolution reaction (OER) or chlorine evolution reaction (CER) was examined by polarization curves. The Tafel slopes for both low (<1.4 V) and high overpotential (>1.4 V) regions were observed. Polarization curves for coatings in 0.5 mol L^{-1} NaCl, 1.0 mol L^{-1} H_2SO_4 and 0.5 mol L^{-1} NaCl + 1.0 mol L^{-1} H_2SO_4 solutions are shown in Fig. 3. The onset potentials (E_{on}) of chlorine and oxygen evolution and the Tafel slope for the two coatings in low overpotential regions are summarized in Table I. Some similar anode materials reported in the literature are also listed as comparisons.

As shown in Fig. 3, the shapes of the polarization curves for the TRL and TR coatings were similar. The polarization currents of the TRL coating were obviously higher than those of the TR coating.

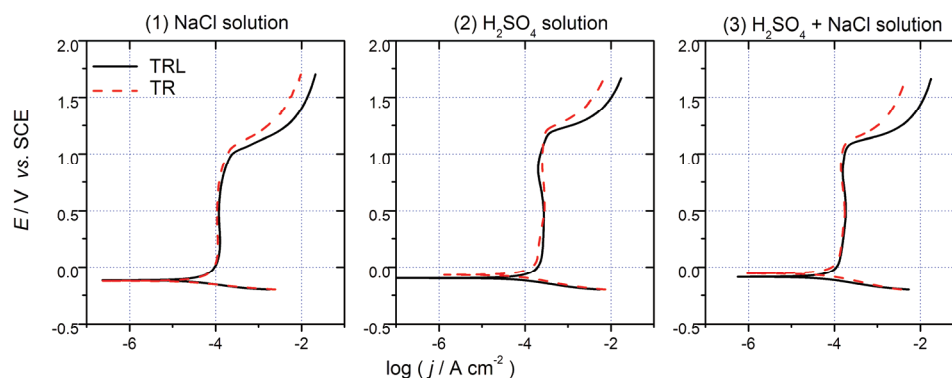


Fig. 3. Polarization curves for TRL and TR coatings in: 1) 0.5 mol L⁻¹ NaCl, 2) 1.0 mol L⁻¹ H₂SO₄ and 3) 0.5 mol L⁻¹ NaCl + 1.0 mol L⁻¹ H₂SO₄ solutions.

TABLE I. Onset potentials (E_{on}) of chlorine or oxygen evolution and the Tafel slope

Sample	Solution	Tafel slope mV dec ⁻¹	E_{on} of CER or OER V vs. SCE	Reference
TRL coating	NaCl	170	1.08	This work
TRL coating	NaCl + H ₂ SO ₄	95	1.10	This work
TRL coating	H ₂ SO ₄	120	1.20	This work
TR coating	NaCl	200	1.12	This work
TR coating	NaCl + H ₂ SO ₄	150	1.11	This work
TR coating	H ₂ SO ₄	170	1.20	This work
RuO ₂ /TiO ₂ /Ti anode	H ₂ SO ₄	60	1.21	2
RuO ₂ /TiO ₂ /Ti anode	NaCl	40	1.08	2
(Ti, Ru, Ir)O ₂ coating	H ₂ SO ₄	180	1.24	24
(Ti, Ru, Ir)O ₂ coating	NaCl + H ₂ SO ₄	100	1.12	24
(Ti, Ru, Ir)O ₂ coating	NaCl	120	0.98	24
Ti/IrO ₂ -Ta ₂ O ₅ anode	H ₂ SO ₄	59	≈1.21	26
RuO ₂ based electrodes	NaCl	40	–	27
10–50mol% RuO ₂ anodes	NaCl	35–40	–	28
30 and 50 mol % RuO ₂ anodes	Na ₂ SO ₄	65	–	28
10mol% RuO ₂ anode	Na ₂ SO ₄	100	–	28
Ti/Ce-nanoTiO ₂ /Ce-PbO ₂ electrode	Na ₂ SO ₄	–	2.1	7

The potential for the chlorine evolution reaction (CER) was 1.08 V for the TRL coating and 1.12 V for the TR coating in NaCl solution. This means that the TRL coating showed higher CER activity than the TR coating. The CER in NaCl+H₂SO₄ solutions occurred in almost the same potential range as in NaCl solution.

In the low overpotential region, the Tafel slopes for the TRL coating were 170 mV·dec⁻¹ in NaCl solution and 95 mV·dec⁻¹ when protons were added into the solution. The Tafel slopes of TR coating were 200 mV dec⁻¹ in NaCl solution

and 150 mV dec^{-1} when protons had been added to the solution. The value of Tafel slope reveals the activity of the coating. The TRL coating, with a lower value of the Tafel slope showed higher electrocatalytic activity than the TR coating. The different Tafel slopes with or without protons in the solution are the result of different reaction mechanisms.^{2,29} The lower values of Tafel slope show that chlorine evolution reaction is easier in the solutions containing both proton and chlorine, because protons are involved in the oxidation of active sites, which creates suitable sites for the adsorption of chlorine gas.^{24,26}

The gas evolution commences at more positive potentials in H_2SO_4 solution than in NaCl solutions and oxygen evolution tends to be at higher overpotentials than those for chlorine. The electrocatalytic activity from such electrodes for oxygen evolution is lower than that for chlorine gas, meaning that oxygen is evolved more slowly than chlorine.

Cyclic voltammetry curves of the TR and TRL oxide coatings at a scan rate 100 mV s^{-1} in 0.5 mol L^{-1} NaCl, 1.0 mol L^{-1} H_2SO_4 , and 1.0 mol L^{-1} H_2SO_4 + 0.5 mol L^{-1} NaCl solutions are shown in Fig. 4. The shapes of the CV curves are typical for DSA-type electrodes.² The oxygen evolution begins at a potential of 1.2 V, and chlorine evolution begins at a potential of 1.1 V. A sharp peak in the potential before -0.2 V is easily identified as hydrogen evolution.

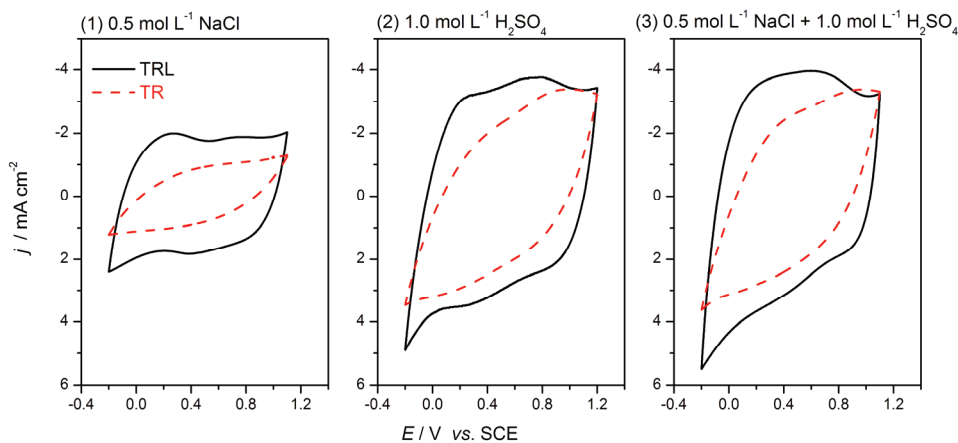
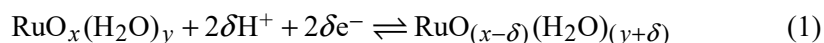


Fig. 4. Cyclic voltammetry curves for TRL and TR coatings in: 1) 0.5 mol L^{-1} NaCl, 2) 1.0 mol L^{-1} H_2SO_4 and 3) 1.0 mol L^{-1} H_2SO_4 + 0.5 mol L^{-1} NaCl solutions.

For the two coatings, capacitive behavior is broader in solutions containing protons (Fig. 4-(2) and 4-(3)) than in NaCl solutions (Fig. 4-(1)), which is because of reversible oxidation–reduction reactions of ruthenium and Ru oxides with the participation of protons. Broad redox peaks appear around 0.7 V, typical for the pseudocapacitive response of the well-developed rutile structure of

RuO₂.² They are recognized as a consequence of proton-assisted solid-state surface redox transitions, that is:



The protons insert into the hydrated structure of the oxide during sweeps at potentials more negative than 0.2 V. The corresponding ejection according to Eq. (1) is extended to rather wide potential range in the subsequent anodic sweep.² Two small pseudo-reversible peaks can be seen at potentials of 0.8 and 0.6 V on the curves for TRL coatings. The observed peaks could be attributed to the oxidation–reduction processes Ru₂O₃/RuO₂ (Ru³⁺/Ru⁴⁺) and Ru₂O₃/Ru (Ru³⁺/Ru), respectively.²¹

The capacitive behavior of TRL is broader than that of TR in all three solutions. The CV responses registered with La-adopted (TRL) coatings show significant increases of the CV currents in comparison to those registered for TR, which indicates oxidation–reduction reactions of ruthenium oxide with the participation of lanthanum oxides. La incorporation causes changes in the coating structure, helping proton insertion into or rejection from the hydrated structure of the oxide.

There is also an improvement in the tilt of the CV curves of La-doped (TRL) coating, suggesting lower internal resistance of the TRL coating than that of the TR coating. This is due to reducing the insulating TiO₂ layer caused by La incorporation into RuO₂.

CONCLUSIONS

La-doped RuO₂-TiO₂/Ti coatings (TRL) and RuO₂-TiO₂/Ti coating (TR) were prepared on the surface of titanium through thermal decomposition. Both the TRL and TR coatings were composed of metallic titanium and two phases, rutile TiO₂ and RuO₂, which is consistent with typical TiO₂/RuO₂ coating. The microstructure of both coatings was similar to cracked mud. The cracked blocks were smaller and rougher in the TRL coating compared with the TR coating, indicating the larger surface area and lower uniformity in composition of the TRL coating.

The electrochemical studying indicated that both coatings showed electrochemical properties typical for activated titanium anodes. The TRL coating showed higher reaction activity with higher polarization currents, lower value of Tafel slope, lower potential of chlorine evolution reaction (CER), broader capacitive behavior and lower internal resistance in comparison to the TR coating. Two small pseudo-reversible peaks, (Ru³⁺/Ru⁴⁺) and (Ru³⁺/Ru), were visible, at 0.8 and 0.6 V, respectively, on the cyclic voltammetric curves of the TRL coating. This confirmed that oxidation–reduction evolution on the surface involve the participation of protons.

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ИЗВОД

СИНТЕЗА И ЕЛЕКТРОХЕМИЈСКА ИСПИТИВАЊА ПРЕВЛАКА $\text{RuO}_2\text{-TiO}_2/\text{Ti}$ ДОПИРАНИХ ЛАНТАНОМ

XIAOYU LIANG¹, SHUAI LI¹, ZHIGANG ZHANG¹, HANG XIAO¹, WEIQIN WU¹, LANG LIN¹, XIAOYUAN WU², WEI LI³, LEI ZHANG³ и WENZHE CHEN³

¹College of Ecological Environment and Urban Construction, Fujian University of Technology, Fuzhou, P. R. China, ²State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, P. R. China и ³College of Materials Science and Engineering, Fujian University of Technology, Fuzhou, P. R. China

Превлака $\text{RuO}_2\text{-TiO}_2/\text{Ti}$ допирана лантаном и недопирана превлака $\text{RuO}_2\text{-TiO}_2/\text{Ti}$ направљене су сол-гел методом и термичким разлагањем, а затим окарактерисане дифракцијом X-зрака (XRD) и скенирајућом електронском микроскопијом (SEM). Електрохемијска својства превлака су испитивана цикличном волтаметријом и поларизационим мерењима издвајања кисеоника и хлора у растворима H_2SO_4 и NaCl . Резултати XRD анализе су указали на малу кристалиничност синтетисаних честица у обе превлаке и да се оне углавном састоје из две рутилне фазе TiO_2 и RuO_2 . SEM анализом је показано да површине обе превлаке имају изглед испуцале земље са блоковима који су раздвојени пукотинама. У случају допираних превлаке блокови су неправилни, што значајно повећава специфичну површину и обезбеђује више активних места. Поларизациона мерења су показала да је потенцијал почетка реакције издвајања хлора на допираној превлаци 1,08 V, што је нижа вредност од 1,12 V која је добијена за недопирану превлаку. Потенцијали почетка реакције издвајања кисеоника су приближно исти на обе превлаке. Цикличном волтаметријом је показано да допирана превлака има већу електрохемијску капацитивност од недопиране превлаке.

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