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Green Synthesis of RuO_2 Electrode for Electrochemical Water Treatment

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Abstract: Nowadays, the electrochemical water treatments are very important methods used for the removal of organic and inorganic impurities from fresh, drinking water and wastewater. The method consists of carrying out the oxidation reaction at the anode where pollutants are transferred into non-toxic substances, by decomposing into simpler compounds or transferring into oxidation form. RuO_2-based Dimensional Stable Anode (DSA) is a technologically good and important electrode for water treatment because of its unique characteristics such as high thermal and chemical stability, low resistivity and low overpotential. This paper reviews the methods for fabricating RuO_2-based electrodes that can be used in electrochemical water treatment. Depending on the different fabrication routes, RuO_2 electrodes will possess the different electro-catalytic property and stability.

Key words: Electrocatalytic, DSA, RuO_2, water treatment.

1. Introduction

RuO_2 is a noble and expensive metal oxide; the price of ruthenium is about 10 times lower than that of platinum [1]. Ruthenium is a chemical element that can easily adopt various formal oxidation states from −II to +VIII in chemical bonds. RuO_2 reveals a complex and unique redox surface chemistry, acting as a versatile oxidation catalyst and electrocatalysis in many applications, especially in water treatment [2]. Roughly 10-15% of the annual production of ruthenium goes into the production of such DSA (in 2010 about 3 tons) while most of the ruthenium is deployed as buffer layers and thin film resistors in the electronic industry (about 20 tons) [3]. For being a well-performing electrode material in water treatment, four major requirements have to be fulfilled: high catalytic activity, high stability, high selectivity and high electric conductivity [4, 5]. There are many methods to fabricating RuO_2 electrodes in industry. The synthesis methods for RuO_2 electrodes should be facile, low cost and environmental friendly.

2. Green Synthesis of RuO_2 Electrode

2.1 Chemical Vapor Deposition (CVD)

For model investigations, a well-defined atomic structure of RuO_2 with a high degree of crystallinity is desirable such as RuO_2 single crystals which can be grown by deposition from the vapor phase. CVD is a synthesis process in which the chemical constituents react in the vapor phase near or on a heated substrate to form a solid deposit [6]. The apparatus is made up with three major components: precursors, their handling reactors and the exhaust of by-products. Fig. 1 represents the CVD process. Most chemical reactions in CVD are thermodynamically endothermic, which means energy has to be supplied to the reacting system. According to the methods of energy input, CVD methods can be categorized into thermal, plasma, photo and acoustic CVD [7]. The reactor consists of a 1.5 m quartz tube with inner diameter of 2.0 cm. At one end, it is connected with the gas inlet, and at the other end, the gas outlet. The inner tube is positioned so that the metal source is at the maximum of the furnace. The gas flow at the inlet is regulated by microvalves and the outlet is evacuated to a fume cupboard. The reactive agents Cl_2, $TeCl_4$ or O_2 are known to carry the

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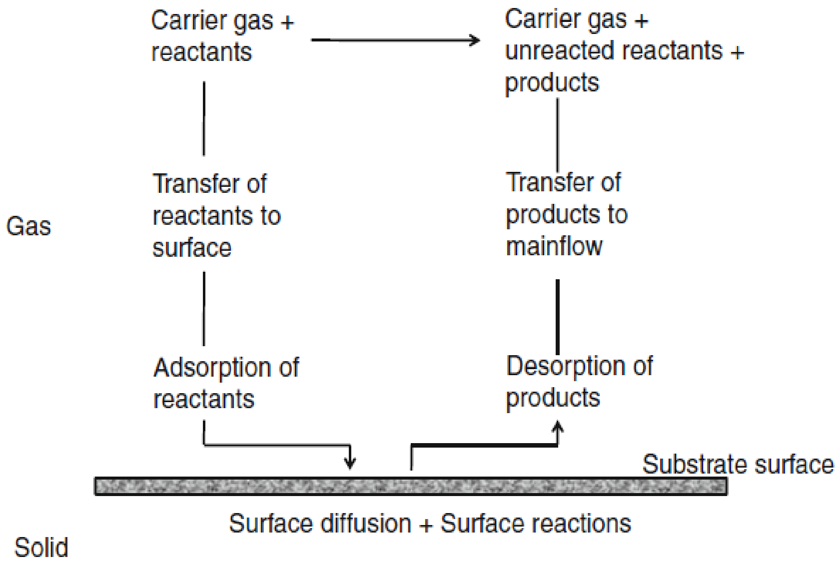

Fig. 1 The chemical processes contributing to CVD growth [6].

components, Ru and O, in the gas phase, forming $RuCl_3$, $RuCl_4$, RuO_3/RuO_4, RuO_nCl_m, etc. with sufficient partial pressures (50 mbar and higher) [7]. In general, O_2 is used as transporting agent. This bears the advantage that only the constituents of Ru-oxides are in the reactor, minimizing the impurity level in the grown RuO_2 single crystals. Oxygen flow (1 bar) is passed over polycrystalline RuO_2 at 1,600 ^oK which results in a (equilibrium) mixture of RuO_3/RuO_4 in the gas phase according to RuO_2 (solid) + $n/2O_2$ (gas) $\leftrightarrow$ RuO_{2+n} (gas) $\rightarrow$ $RuO_2(s) + O_2(g)$. The outlet zone of the reactor is kept at a lower temperature, say 1,450 ^oK, where the gas mixture of RuO_3/RuO_4 decomposes and RuO_2 crystallizes in the form of 1-3 mm thick blue-black plates (up to 6×10 mm^2). The (101) facet is present on most of the growth habits and appears to be the predominant orientation, followed by the (100) and (110) faces. In order to use these crystals in surface science, the sample has to be heated in a vacuum above the decomposition temperature (about 1,000 ^oK) resulting in an ultrathin metallic layer capping the RuO_2 crystal. The vapour growth of these oxides is based on the fact that the higher oxides RuO_3, RuO_4 exist as vapour at high temperature and decompose to give RuO_2 at lower temperature [8-10].

Metal organic chemical vapor deposition (MOCVD) provides another method to form thin RuO_2 films. However, these films suffer sometimes from carbon contamination. With this method, conductive RuO_2 films could be prepared either with (110) or with (101)-textured orientations on SiO_2/Si (001). The structural texture of the RuO_2 films can be controlled by both temperature and growth rate. The roughness of MOCVD-grown RuO_2 films can be reduced by codeposition of iodine containing molecules. Very clean thermally stable Ru films can be produced by chemical vapor deposition (CVD) using RuO_4 or hydrous-RuO_2 as the metallic precursor. As a Ru precursor, Ru-carbonyls are frequently used and the actual oxidation process is assisted by oxygen plasma [11-14].

2.2 Thermal Decomposition

DSA-type metal oxides can be prepared in various ways, but the most applied procedure in technology is the thermal decomposition of appropriate precursors, mainly $RuCl_3$ salts, dissolved in suitable solvents and painted on the metal substrates, mainly titanium and firing the deposit in air or oxygen at 450 ^oC [6]. The thermal decomposition method is preferred, due to its specialties of simple conduction and low cost. The painting and firing procedure usually repeated some 10-12 times to produce a relatively thick conducting film. Oxide electrodes prepared by thermal decomposition of suitable precursors consist of porous layers of sintered crystallites [6]. Fig. 2 shows the schematic diagram for the metal-oxide electrodes fabrication process with thermal decomposition methods. Pretreatment on the metal substrate should be conducted before thermal deposition, in order to enhance the adhesion of produced metal oxide on the substrate. Normally, pretreatment process includes: first, thoroughly cleaning of the substrate by organic solvent and degreasing agent and second, etching of the substrate in concentrated HCl at high temperature for 30 min to 1 h, to remove the original surface oxides and increase the surface roughness. The chemical composition, crystallinity and crystal grain size, surface morphology, electrical conductance, electrocatalysis performance, and electrode stability are determined by the precursor composition, solvents and loadings, substrate pretreatment, and thermal decomposition parameters especially the temperature and duration of the preparation and calcinations processes [15]. It is reported that RuO_x exists with the largest amount when annealed at around 450 ^oC, and disappears at 600 ^oC [16]. Furthermore, the morphology of the active layer changes with the calcinations temperature and loading level of the catalyst. The slight increase in chlorine evolution currents with increasing oxide annealing temperature is probably due to a small increase in cracks and external surface area (Fig. 3) [7]. Porosity and crystallite size depend on the calcinations temperature. SnO_2 is frequently used as an additive in industrial RuO_2-based electrodes to enhance their selectivity for chlorine evolution with respect to oxygen evolution [7]. In a recent paper, the chlorine evolution and oxygen evolution were studied on well-defined RuO_2 nanocrystals with a typical size of 10-50 nm [17].

2.3 Sol-gel

Both thin and thick RuO_2 coatings on Ti substrate can be produced by the sol-gel process. Typical film thicknesses achieved are several 100 nm after calcinations at 450 ^oC for 2 h. An approach based on the attractive sol-gel route for the preparation of noble metal oxides seems to be promising both electrocatalytic and stability with oxygen, chlorine evolutions. It has been suggested that electrocatalytic properties and stability of DSA can be significantly improved if the active coating is prepared by a sol-gel procedure, as an alternative to the commonly used preparation procedure that involves thermal decomposition of metal chlorides [18]. The improvement is due to an enlargement of the active coating surface area and increased contribution of the so-called geometric catalytic factor caused by the formation of finely dispersed oxide particles during the sol-gel procedure. The electrochemical behavior for the chlorine evolution depends sensitively on the aging time of RuO_2 and TiO_2 sols [19]. A typical cracked-mud morphology of a RuO_2-based DSA is depicted in Fig. 4 [19]. The formation of "cracks" in a catalytic layer during synthesis is typically achieved by inducing a large enough tensile stress in the layer. During the process of sol-gel synthesis, a wet layer of

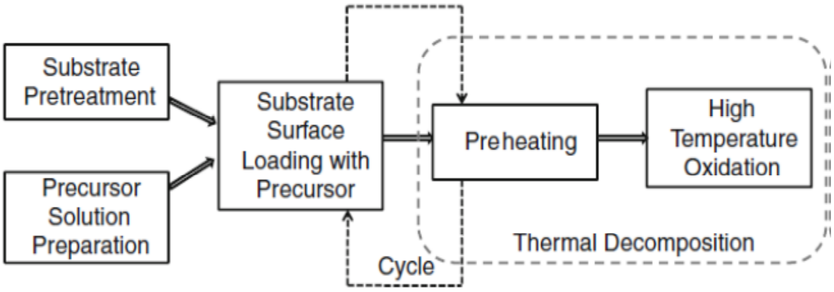

Fig. 2 Schematic diagram of thermal decomposition method for making DSA type electrodes [6].

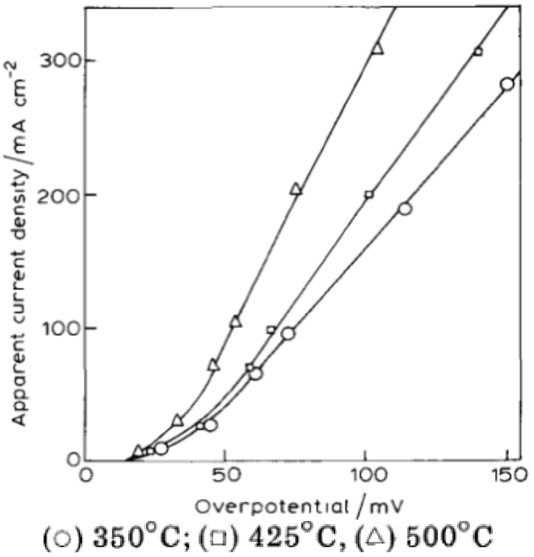

Fig. 3 Current-voltage plots for chlorine evolution in 5 M NaCl + 0.1 M HCl [7].

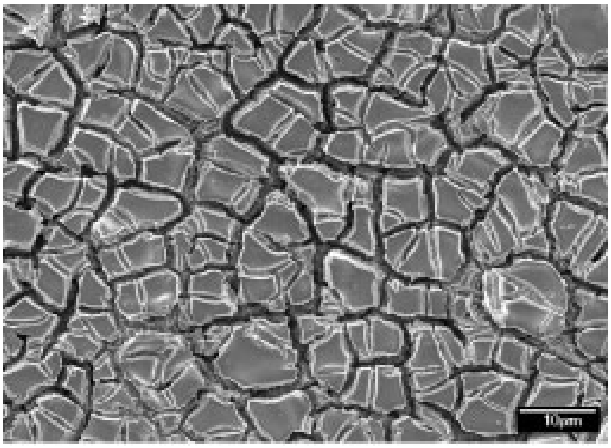

Fig. 4 A typical cracked-mud morphology of a RuO_2-based DSA [19].

salt precursors of the catalyst is deposited on a solid substrate. After drying, the catalyst is exposed to thermal annealing to transform it into the active state. The volume change of the gel-body during the drying and thermal treatment steps is restricted by the substrate, which results in an internal stress that depends on the density change of the coating during drying and the mismatch in the coefficients of thermal expansion between thin coating and thick substrate. If the internal stress is large enough, surface cracks or channel cracks may nucleate and release energy. The rutile-type solid solution of RuO_2 and TiO_2 is responsible for the catalytic activity and the electrochemical stability [20]. Recently, Chen et al. [21] synthesized a novel structure of coating which consists of active nanocrystals of rutile RuO_2/TiO_2 supported on anatase TiO_2. Anatase TiO_2 stabilizes the high dispersion and inhibits the growth and agglomeration of active rutile particles. A common difficulty encountered in the preparation [21]. The erosion rate is minimal around pH = 1-2, and it increases below pH = 0.2 due to formation of $RuOHCl_5^{2-}$ and increases above a pH value of 4 due to the mixed oxides electro coatings ensuring a single phase structure and nanoscale catalysts [6]. Owing to the controlled hydrolysis and polycondensation reactions, sol-gel synthesis of mixed oxides has shown to be superior to other synthesis techniques [22]. Crack-free $Ru_{0.25}Ti_{0.75}O_2$ coatings have shown to be more long-term stable, revealing however lower catalytic activity [23].

2.4 Reactive Sputtering

In reactive sputtering, the total pressure with O_2 concentration often shows hysteresis behavior. According to a well-accepted model for reactive sputtering, the disappearance of the hysteresis is caused by the high reactive gas pumping speed of the high vacuum pump compared with the gas consumption by the target, substrate and walls [24]. Ultrathin Ru (0001) films can be deposited on Si (001) by magnetron sputtering and subsequently be oxidized at various temperatures, exposing molecular oxygen, ozone, NO_2 or plasma-activated O_2. To deposit RuO_2 thin films on dissimilar substrates, sputtering is the most commonly used technique. O_2 containing plasmas are frequently utilized for Ru etching [25, 26]. In the same system and at the same partial pressure of argon, a hysteresis was obtained while sputtering titanium in an Ar-N_2 mixture. Slow ruthenium oxidation limits the power that can be used in reactive sputtering of RuO_2. Therefore all depositions were made using 250 W, R_{avg} was in the range 0.5-0.6 nm·s^{-1}. RuO_2 films were deposited by d.c. reactive sputtering in an in-line sputtering system on a dynamic substrate in an $Ar\text{-}O_2$ atmosphere. Annealing RuO_2 films at 350 °C in air improved their crystallinity, resulting in better matching with the rutile structure. The resistivity of RuO_2 depended on the O_2 concentration in the sputtering atmosphere. The resistivities of the most conductive as-deposited and annealed films were about 300 μΩ·cm and 200 μΩ·cm. Transmittance and reflectance of RuO_2 films in the IR region had a metallic character. The Drude model was applied to the dielectric constants in the spectral range of 1.4-0.65 eV. Plasma energies of 4.7 eV and 5.5 eV and an electron relaxation time of $(4q^5) \times 10^{-14}$ s were found for the annealed RuO_2 films. RuO_2 films can be prepared by reactive r.f. sputtering in an O_2-Ne gas mixture over a wider range of sputtering conditions than by sputtering in O_2-Ar. This property makes reactive sputter deposition in an O_2-Ne ambient a process that is easy to control. The Ru etching rate can be increased by Cl_2 addition to O_2 plasma. Magnetron plasma sputtering or even better reactive sputtering in O_2 atmosphere produces RuO_2 films with a Ru/O film stoichiometry of 1:2. These oxide films are in general polycrystalline with the typical nanorod morphology, although it is also possible to produce X-ray amorphous RuO_2 films, depending on the substrate temperature [27-29].

2.5 Electrodeposition

Electrodeposition has proved to be a simple, versatile, one-step and cost effective method with film thickness control for electrode preparation [30-36]. The two key mechanisms that have been identified as the rate determining steps for crystal formation are charge transfer and diffusion of supersaturated ions or mass transport at the electrode surface. With cathodic electrodeposition, metal ions can be precipitated in the form of amorphous oxide and hydroxides which are transformed into the crystalline oxides by subsequent thermal treatment. Zhitomirsky succeeded first in the simultaneous electro-deposition of TiO_2 and RuO_2 onto a Ti plate in the form of a mixed oxide layer [37]. Since the electrodeposited films are thicker than those produced by painting, fewer calcinations steps are required to produce a similarly thick DSA coating. The electrodeposition of a metal oxide proceeds via a wet chemical precipitation induced by a cathodically electro-generated base seem very promising [6]. This method produces typical morphology with an increase of the specific outer surface area, which is the main working part during intensive chlorine gas evolution [23]. A titanium wire (Goodfellow Metals, 99.9% purity, 0.25 cm^2 geometrical area) sealed in glass served as a substrate for electrodeposition. It was polished with emery paper and alumina powder, washed with quadruply distilled water. The electrodeposition route for a metal oxide preparation uses a cathodic reaction to increase the pH locally near the electrode surface. The main cathodic reaction to produce OH^- is the decomposition of water under hydrogen evolution as followed reactions [38, 39]:

$$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^- \quad \text{(Reaction 1)}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \text{(Reaction 2)}$$

These reactions consume H_2O, generate OH^- and increase pH at the cathode. In cathodic deposition, metal ions or complexes are hydrolyzed by electrogenerated base to form oxide, hydroxide or peroxide colloidal particles deposits on cathodic substrates. Hydroxide and peroxide deposits can be converted into corresponding oxides by thermal treatment. The assumed reactions can be represented as:

$$Ru^{3+} + OH^- \rightarrow RuO_x(OH)_y \rightarrow RuO_2 \quad \text{(Reaction 3)}$$

The cathodic decomposition of water can be competed with the cathodic electro-deposition of Ru metal:

$$Ru^{4+} + 4e^- \rightarrow Ru \quad \text{(Reaction 4)}$$

The anodic electrodeposition of ruthenium was carried out galvanostatically from a stirred solution of 1 $g\cdot dm^{-3}$ $RuCl_3$, 0.1 M HCl (Fluka, puriss.) at a current density of 40 $mA\cdot cm^{-2}$ for 15 min at room temperature or treated by a potentiodynamic sweeps from -0.2 V to +1.2 V us see at 2 Hz for 2 min in 0.5 M H_2SO_4.

3. Conclusions

RuO_2-based Dimensional Stable Anode is a technologically good and important electrode for water treatment because of its unique characteristics such as high thermal, chemical stability, low resistivity and low overpotential. There are many green synthesis routes for the preparation of RuO_2 electrode for water treatment. Depending on the different fabrication routes, RuO_2 electrodes will possess the different electro-catalytic property and stability. Thermal decomposition and sol-gel are the most common methods to prepare RuO_2 electrodes.

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