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Manganese-Containing Mixed Oxide Electrodes as Anode Materials for Degradation of Model Organic Pollutants

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Mixed oxide thin film electrodes have been prepared by thermal decomposition from alcoholic solution on Pt substrate. In particular, three different anodes have been obtained by co-deposition of Ru (Ruthenium) and Mn (Manganese) oxides, Ru, Mn and Cu (Copper) oxides and co-deposition of Ru, Mn and Co (Cobalt) oxides.

The electrochemical behaviour of the prepared electrodes was evaluated by potentiodynamic polarization curves and cyclic voltammetry tests. We also tested and compared their oxidizing ability in the degradation of aqueous solutions containing methyl orange as model compound and small amount of chloride. Galvanostatic experiments were conducted in a membrane-free reactor. The treatment extent was assessed by detection of color and TOC decay. The electrogeneration of active chlorine, chlorate and perchlorate was also monitored. The preliminary results show that ternary oxides coated electrodes exhibit enhanced electrocatalytic activity without producing undesired chlorinated by-products.

1. Introduction

The application of electrochemical technologies is strongly influenced by the availability of efficient, stable and durable electrodes. For this reason, great effort has been devoted to the development of innovative materials with enhanced performance. An interesting group of anodes is represented by those named Metal Mixed Oxide electrodes (MMOx) consisting of an electrocatalytic thin film of noble metals oxides coating a Platinum or Titanium support. To extend the electrode lifetime while maintaining same electroactivity, different catalytic coating formulas have been designed and tested over the years (Trasatti et al., 1980).

In particular, ruthenium oxide-based electrodes have exhibited excellent electrocatalytic characteristics for chlorine evolution (Burrows et al., 1978). During electrolyses of chloride-containing solutions they result in the electrogeneration of a mixture of oxidants named active chlorine with high disinfection power (Jeong et al., 2009). The production of chlorates, even if in lower amount than other electrodes such as boron doped diamond anode (Bergmann et al., 2009), also occurs. Before disposal, the residual amount of these chlorination by products have to be removed with additional cost and hazard. Therefore, to reduce the impact of the electrochemical treatment, the electrogeneration of these compounds have to be mitigated.

In particular, our research group have evaluated the possibility of fabricating multilayer electrodes consisting of a MnOx thin film grown on a RuOx film deposited on a titanium substrate (Sotgiu et al., 2014). The addition of manganese to ruthenium is attractive to diminish both cost and toxicity of these materials. Other papers report the use of mixed oxides of manganese and ruthenium but for different purposes. For instance, electrodes were prepared for electrochemical capacitor (Wen et al., 2009) or for oxygen evolution reaction (Browne et al., 2016).

The results we obtained in the anodic oxidation of organic pollutants and the comparison with the surface composition, showed that the co-presence of the two oxides on the electrode surface did improve the electrocatalytic performance while limiting the production of inorganic chlorinated species (Sotgiu et al, 2015). This behaviour, attributed to a delay in the chlorine evolution due to the presence of manganese, was affected by the preparation route of thin films (Sotgiu et al., 2014) and by the miscrostructure of the supporting surface (Sotgiu et al., 2015).

In this study, the fabrication of platinum electrodes coated by thin films composed of mixed ruthenium and manganese oxides is presented. The effect of the co-presence of a third electroactive metal such as copper or cobalt in the mixture was investigated. The electrochemical characterization via cyclic voltammetry and potentiodynamic polarization curves is provided. Their applicability in the anodic oxidation of a solution containing a model dye (i.e. methyl orange) was discussed. During the electrolyses, samples were withdrawn at selected times and analysed for methyl orange, active chlorine, chlorates and perchlorates content. The mineralization efficiency was assessed by total organic carbon (TOC) measures at the end of the treatment.

2. Experimental

2.1 Materials

Reagents were supplied by Sigma Aldrich and used without any further purification.

Sample solutions were prepared by dissolving in distilled water 50 mg L^{-1} of methyl orange ($C_{14}H_{14}N_3NaO_3S$, MW 327.33 g mol^{-1}), 0.05 M Na_2SO_4 and 0.01 M NaCl. The initial TOC value was about 28 mg L^{-1}.

2.2 Electrode preparation

The Platinum support (rectangular shape of 0.5 cm x 1.8 cm) was fine sanded and then rinsed by ultrasonic washing for 10 minutes with double distilled water and then with acetone. The mixed oxides layer was prepared by thermal decomposition, by painting alcoholic solutions on one side of the electrode. The electrodes were then calcinated in a muffle furnace for 10 min at 400°C. The treatment was repeated three times followed by a final 1 hour treatment at 400 °C.

As salt precursor we used 0.1 M $Mn(NO_3)_2$ in ethyl alcohol; 0.1 M $RuCl_3$ in isopropylic alcohol; 0.1 M $CuSO_4 \cdot 5H_2O$ in methyl alcohol; 0.1 M $Co(NO_3)_2$ in ethyl alcohol. The electrodes were prepared using mixtures containing equimolar ratios. The experiments reported in this study were performed by using the three electrodes illustrated in Figure 1.

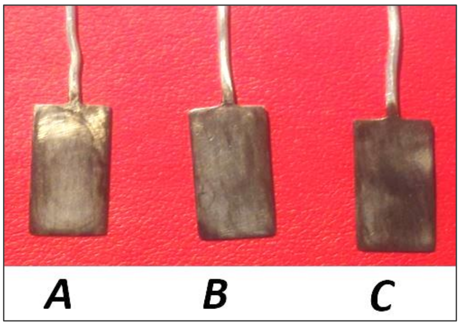

Figure 1: Image of the electrodes used in the study: A) RuOx-MnOx electrode, B) RuOx-MnOx-CoOx electrode, C) RuOx-MnOx-CuOx electrode.

2.3 Electrode characterization

Potentiodynamic polarization tests were conducted with a Amel 5000 potentiostat/galvanostat. The experiments were carried out using an undivided cell with Ag/AgCl electrodes (saturated KCl) as reference and Pt wire as counter electrode. The scan rate was 2 mV/s commencing at a potential of 250 mV below the stable open circuit potential. Before starting the measurements the specimen was left to attain a steady state (5 minutes at OCP) which was indicated by a constant potential. The tests were conducted in aqueous solutions containing 0.5 M Na_2SO_4 and 0.01 or 0.05 M NaCl.

Cyclic voltammetry (CV) experiments were performed at room temperature with a three-electrode cell of 10 mL volume consisting of the in-made anode, a Pt sheet as the counter electrode and a Ag/AgCl electrode (saturated KCl) as reference electrode. A AMEL 5000 potentiostat was used. The scan rate was 50 mV/s and scan range was from 0 to +1.6 V. Where reported, the chloride concentration in solution was varied by adding NaCl.

2.4 Electrochemical degradation of methyl orange solutions

Galvanostatic experiments were performed with a AMEL 2051 potentiostat at a current density of 300 A m^{-2} in an undivided glass reactor. The cell was magnetically stirred and thermostated at 20 ± 2 °C. A rectangular Pt foil was used as the cathode. As the anodes, we tested the three mixed oxide electrodes. Their performances were compared to that of a same-size boron doped diamond electrode BDD (Adamant Technologies). All the electrodes had a surface area of 0.9 cm^2. The sample volume was 35 ml thus resulting in a volume to electrode surface ratio of about 40.

2.5 Analytical methods and equipment

pH was measured by using a Crison GLP 421.

The color removal was assessed by measuring the absorbance decrease at the maximum wavelength (463 nm) with a PG Instruments T80+ UV/Vis spectrophotometer.

The active chlorine concentration was determined using the DPD (N,N-diethyl-p-phenylenediamine) reagent by colorimetric method at 510 nm wavelength.

Anions were quantified using a Dionex 120 ion chromatograph equipped with suppressed conductivity detection. An IONPAC AS12A anionic column used with isocratic carbonate/bicarbonate eluent was adopted for the determination of chlorate. The flow rate was 1.5 mL min^{-1}. The detection limit was 100 μg L^{-1}.

The removal efficiencies of color and TOC removal were calculated using the following formula, where x_0 and x_t represent the initial and remaining value of the x variable at a given time:

$$R\ (\%) = \frac{(x_0 - x_t)}{x_0} * 100$$

3. Results and discussion

Figure 2 shows the polarization curves of the different electrodes. The corrosion potential (E_0) and corrosion current (I_0) extrapolated from the plots are listed In Table 1.

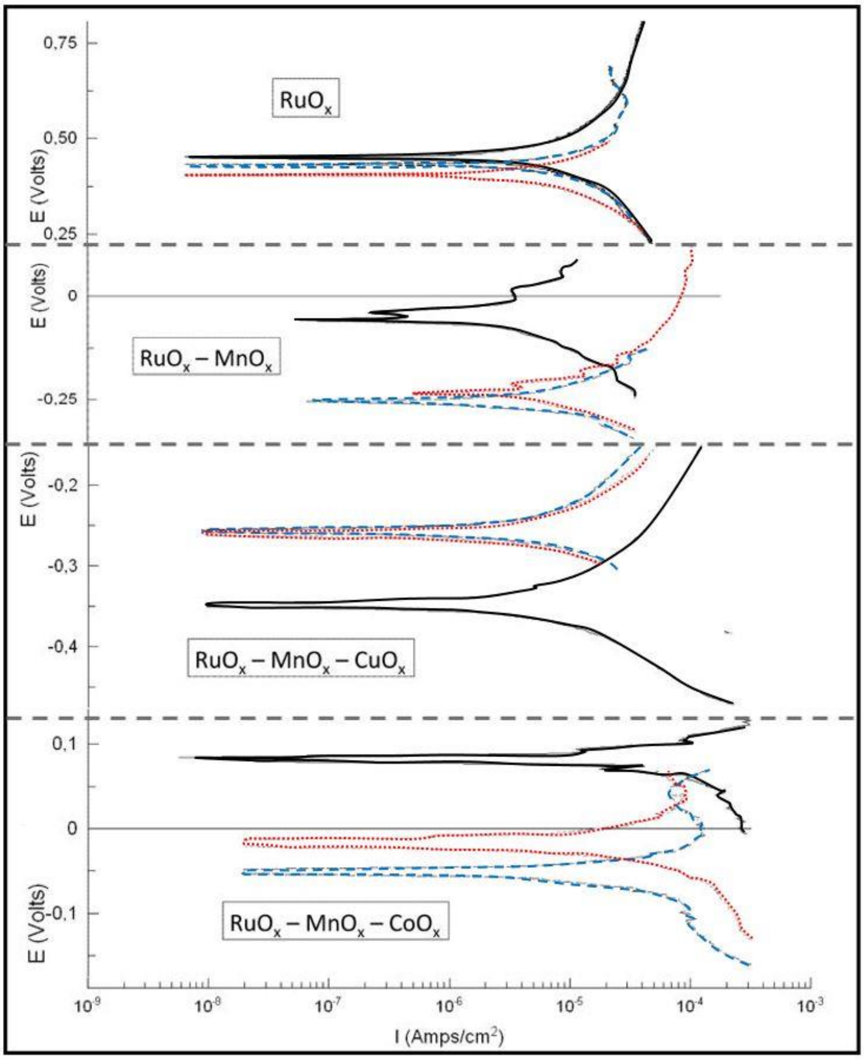

Figure 2: Potentiodynamic polarization curves of the different electrodes obtained at 20 °C without (black lines) and with 0.01M (- - - -) and 0.05M (— — —) chloride. [vs. Ag/AgCl sat., scan rate = 2 mV/s].

Table 1: Parameters obtained from potentiodynamic polarization curves of the prepared electrodes.

	RuOx			RuOx-MnOx			RuOx-MnOx-CuOx			RuOx-MnOx-CoOx		
Cl^- (M)	0	0.01	0.05	0	0.01	0.05	0	0.01	0.05	0	0.01	0.05
I_0 (10^{-5} A cm^{-2})	1.507	2.076	3.106	7.237	12.33	5.584	19.21	6.266	4.809	1.043	2.132	2.750
E_0 (V)	0.451	0.404	0.432	-0.063	-0.242	-0.268	-0.360	-0.256	-0.241	0.083	-0.021	-0.052

The RuOx anode presented a positive value of corrosion potential (about 0.4 V) that remained unaffected by the presence of chloride. The addition of Mn to Ru, varied significantly the electrode characteristics. The corrosion potential shifted to negative values; the material was then more easily oxidizable. This behavior was magnified by addition of chloride.

The addition of copper and cobalt resulted in different behavior. The presence of copper in the metal mixed oxide film caused a shift of the corrosion potential (E_0) to more negative values while the opposite effect was observed in the presence of cobalt. Cobalt exhibited a behavior similar to manganese but with enhanced effect of chloride concentration.

Cyclic voltammogram of the copper-containing electrode (Figure 3 a), in the absence of chlorides, exhibits a sharp peak at 0.4 V and a broad peak at 0.6 V that can be presumably attributed to reactions involving the constituent oxides. The addition of chloride, reduced significantly the peaks intensity and resulted in a shift of the water discharge to higher potential values (+ 0.3 V). Furthermore, under these conditions, a decrease in the voltammetric area and therefore in the presumable electroactivity of the electrodes, was observed. This could be ascribed to the occurrence of surface interactions between the mixed oxides and chloride ions.

Differently, voltammetric curves of the cobalt-containing electrode (Figure 3 b), did not show anodic peaks and only a slight shift of the solvent discharge potential was observed in presence of chloride. Moreover, not significant differences in the voltammetric areas were verified.

Some cathodic peaks of difficult attribution can be observed. In particular, in the presence of chloride both the electrodes they exhibit a cathodic peak at 0.3 V that can be ascribed to the reduction and/or desorption of the chlorine oxidation products, probably hypochlorite.

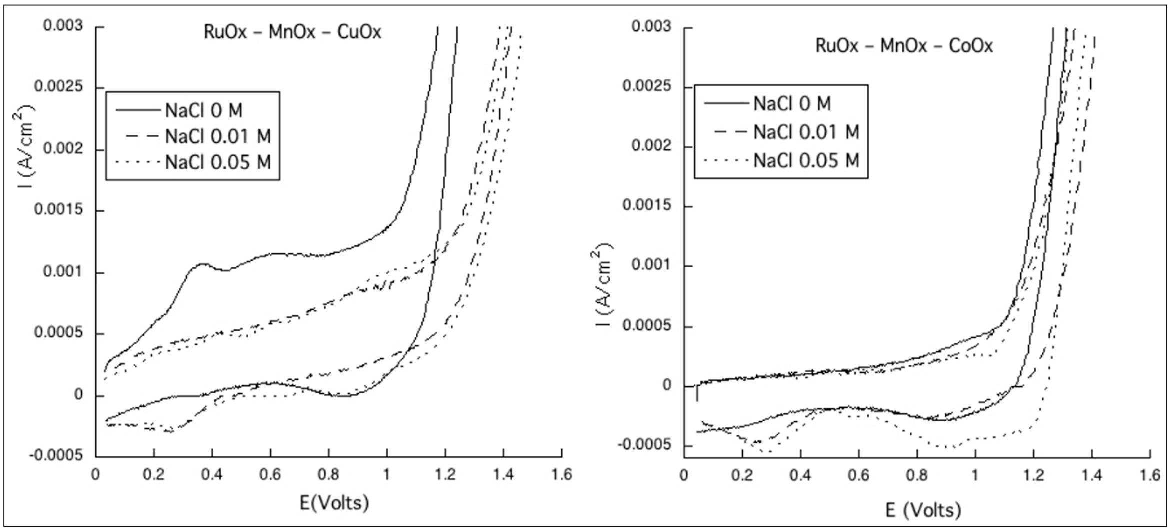

Figure 3: Cyclic voltammograms of RuOx-MnOx-CuOx electrode (a) and RuOx-MnOx-CoOx electrode (b). Conditions: 0.5 M Na_2SO_4 and 0.01 M NaCl [vs. Ag/AgCl sat., scan rate = 50 mV/s].

The behaviour of the prepared electrodes in the anodic oxidation of organic compounds was evaluated by means of galvanostatic electrolyses of 50 mg L^{-1} Methyl Orange solution with 0.05 M Na_2SO_4 as supporting electrolyte. 0.01 M of chloride was added in the solution in order to study the oxidation mediated by electrogenerated active chlorine. The UV-Vis spectrum of untreated Methyl Orange solution (Figure 4) exhibited a broad peak at 463 nm that can be attributed to the conjugated structure of substituted azobenzene connected by means of a diazo group and a weak peak at 270 nm typical of phenolic compounds. During electrochemical degradation the visible peak progressively disappeared with a rate dependent on the anode adopted as well as on current density and initial chloride concentration (data here not reported). The UV region peak, instead, undergoes a shift to lower wavelength (247 nm) attributed to sulfanilic acid formation (Yang et al., 2016). The intensity of this new peak reached a maximum after 30 minutes and then slowly decreased thus indicating that sulfanilic acid is an intermediate of the MO oxidation. The accumulation of this by-product was due to the slow oxidising power of the system that can be partially attributed to the operative conditions. In fact, in these experiments a high value of sample volume to electrode surface ratio, was adopted. More efficient process could be easily achieved by using larger electrode or by diminishing the treated volume.

In spite of this consideration, almost complete discoloration of the solution was obtained after 2 hours of treatment with all prepared electrodes even if with different efficiency. Increasing speed in color removal was observed when using RuOx-MnOx, RuOx-MnOx-CuOx and RuOx-MnOx-CoOx electrode (Figure 5). In particular, a 90% colour removal was obtained after 52 minutes with RuOx-MnOx, 40 minutes with RuOx-MnOx-Cu and only 34 minutes with RuOx-MnOx-CoOx electrode.

It is generally accepted that color removal in dying solutions is promoted by selective attack of chromophoric group by active chlorine (Montanaro and Petrucci, 2009). Therefore, we hypothesized that the different behaviour of our electrodes was related to their different ability to electrogenerate this mixture of oxidizing species via oxidation of chloride ions. In fact, as reported in Table 2, the amount of residual active chlorine after a 2-hour treatment was higher for RuOx-MnOx-CuOx and RuOx-MnOx-CoOx electrodes.

The TOC decay of MO solutions, measured only at the end of the treatment (Table 2) are rather low for all electrodes as expected by spectra analysis showing high absorbance value in the UV region. In particular, also TOC removal, RuOx-MnOx electrode showed the worst performance while RuOx-MnOx-CuOx presented a mineralization ability superior than RuOx-MnOx-CoOx in contrast with the result obtained in color removal tests. It is worth noting that no chlorates were ever detected. A comparison with a same size BDD anode resulted in faster colour and TOC removal (complete decoloration after 30 minutes and about 43% mineralization after 2 hours). However, under the conditions adopted, at the end of the electrolysis we detected 46 mgL^{-1} of residual active chlorine and approximately 150 of chlorate mgL^{-1}.

Low and almost constant cell potential values (3.8± 0.3 V) were detected during all the treatments thus indicating a good chemical and electrochemical stability of the prepared electrodes.

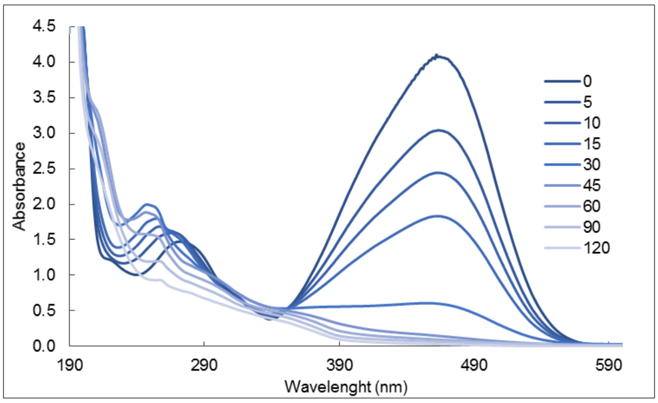

Figure 4: Evolution of UV-Vis spectra of methyl orange solutions treated with Mn-Ru-Co anode. Conditions: 50 mg L^{-1} methyl orange, 0.01 M NaCl, 0.05 M Na_2SO_4, j=300 A m^{-2}.

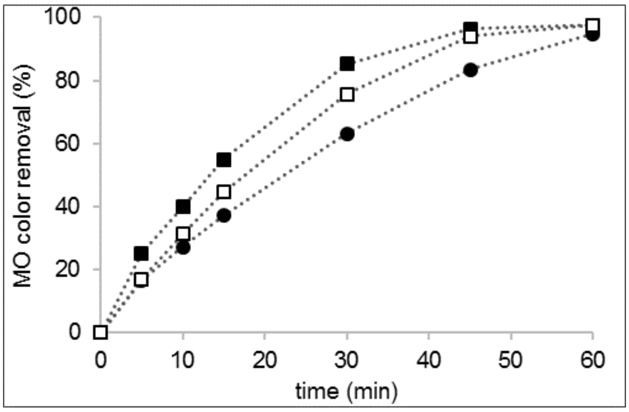

Figure 5: Performances of anodic material (● Mn-Ru, □ Mn-Ru-Cu, ■ Mn-Ru-Co) in color removal of methyl orange (MO) solution. Conditions: 50 mg L^{-1} methyl orange, 0.01 M NaCl, 0.05 M Na_2SO_4, j=300 A m^{-2}.

Table 2: Residual active chlorine, chlorate and TOC removal after 2-h electrolysis of methyl orange solution. Conditions: 50 mg L^{-1} methyl orange*, 0.01 M NaCl, 0.05 M Na_2SO_4, j=300 A m^{-2}.*

Anode	Active Chlorine (mg L^{-1} Cl_2)	Chlorate (mg L^{-1} ClO_3^-)	TOC removal (%)
Mn-Ru	11.98	n.d.	20.8
Mn-Ru-Cu	20.97	n.d.	26.6
Mn-Ru-Co	22.47	n.d.	23.3
BDD	46.35	152	43.1

4. Conclusions

RuOx-MnOx thin films electrodes for anodic oxidation of aqueous solution containing azo dye were produced and characterized. In the presence of small concentration of NaCl, all electrodes exhibited good decolorization but limited TOC removal, if compared to a BDD electrode.

The co-presence of other metals, in a ternary oxide mixture, improved the electrocatalytic performance of the anodes. In particular, the addition of cobalt results in increased production of active chlorine and fast color removal. The addition of copper slightly improved the mineralization extent.

The analysis of UV-Vis spectra supports the hypothesis of a similar degradation pathway involving the rapid attack of the chromophore followed by formation of persistent intermediates.

Under the conditions adopted, the electrogeneration of chlorate was negligible thus supporting further development of these electrodes for the treatment of pollutants in chloride-containing medium.

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