Effect on durability and electrochemical response of the addition of a non-noble transition metal in mixed Ruthenium and Manganese oxide thin-film electrodes

Giovanni Sotgiu[a], Monica Orsini[a], Serena De Santis[a], Francesco Porcelli[a], Elisabetta Petrucci[b*]

[a] Department of Engineering, Roma Tre University, Via Vito Volterra 62, 00146 Rome, Italy
[b] Department of Chemical Engineering Materials & Environment, Sapienza University of Rome, Via Eudossiana 18, 00184 Rome, Italy
*elisabetta.petrucci@uniroma1.it

Mixed metal oxide (MMOx) thin films-based electrodes have been widely used in the treatment of polluted solutions. To limit costs while exploring new electrocatalytic potentials, novel mixtures are being proposed.
In this paper, the electrochemical behavior of thin films obtained by co-deposition of Ruthenium, Manganese, and a third transition metal among Copper, Iron, and Cobalt was investigated with the scope of finding optimal compositions and long stability for applications as the anodes in environmental treatments.
The binary and ternary oxides coated electrodes were prepared by thermal decomposition on titanium foils from alcoholic solutions.
The morphological properties of the thin films were analyzed through scanning electron microscopy (SEM) while the electrochemical performance was evaluated by potentiodynamic polarization curves and cyclic voltammetry (CV). The service time was assessed by accelerated life tests.
The results show that the combination of Ruthenium with one or two different metals results in evident modifications of the morphology, both kinetic and thermodynamic electrochemical properties as well as the service lifetime.
In particular, a combination of Iron and Manganese was to be excluded because of the poor solubility which affected both the coating homogeneity and electrochemical response. The Cobalt-containing electrodes outperformed the others in terms of stability. The addition of Copper implied a reduced susceptibility to corrosion and higher charge storage.

1. Introduction

Metal oxide electrodes have been extensively studied for their electrocatalytic properties, fast ion transfer kinetics, and high electrical conductivity. Most of their properties can be attributed to their multiple oxidation states. These materials have been widely investigated either as electrodes for electrochemical treatments (Wu et al., 2014) or as electrochemical capacitors (Delbari et al., 2021).
Typically, the mixtures include a noble metal, such as Ruthenium or Iridium, with noble or, preferably, non-noble transition metals both to reduce the cost and to tailor materials with different electrochemical properties.
Ruthenium, either as an interlayer (Sotgiu et al., 2014) or in a mixed oxide mixture (Petrucci et al. 2018), has been commonly combined with Manganese.
Mixed Manganese–Ruthenium oxides electrodes, due to easy production, electrocatalytic activity, supercapacitive behavior (Lei and Chen, 2015), mitigation of dangerous by-products (Petrucci et al., 2018), and decreased overpotential for oxigen evolution reaction (OER) (Browne et al., 2016), have been recently tested in a broad range of applications with promising results.
The main drawback is related to the partial solubilization of the coating that can be improved by appropriate modification of the substrate surface (Sotgiu et al, 2015).

Relatively few ternary combinations have been so far investigated and most of them still contain elements of the platinum group. For example, solid solutions containing Ruthenium, Titanium, and Iridium have been tested in the anodic oxidation of wastewater (Santos et al., 2016) and the evolution of chlorine from seawater (Moradi and Dehghanian, 2014). However, conflicting outcomes were obtained. In the first case, the performance was similar to that obtained by using a binary solution with only Ruthenium and Titanium while in the second case, the ternary mixture resulted in an extended lifetime of the materials. Further extension of the service time was also observed by replacing TiO_2 with SnO_2 (Vazquez-Gomez et al., 2006). Other successful attempts were made to produce ternary coatings including Ruthenium, Antimony, and Tin oxides (Chen et al., 2011) where RuO_2, SnO_2, and Sb_2O_5 were found to act, respectively, as the catalyst, the dispersing agent, and the dopant.

In the present work, to further explore the possibility to tune the electrochemical properties of Ruthenium-based films, different mixed oxide coatings were co-deposited on Titanium, by thermal deposition. A series of binary mixed electrodes formed with Ruthenium and one additional metal among Manganese, Copper, or Iron (nominal molar composition of 1: 1) was prepared. Furthermore, a series of ternary electrodes presenting the same nominal concentration of Ruthenium (50%) and the rest consisting of a mixture with different ratios of Manganese and a third transition metal among Copper, Iron, and Cobalt were also fabricated.

The morphology and electrochemical properties as well as the stability of the prepared electrodes were characterized and compared to identify the effect of each element on the material performance. Finally, the stability of the films was investigated by accelerated lifetime tests.

2. Experimental

2.1 Materials
All reagents were supplied by Sigma Aldrich and used as received.

2.2 Electrode preparation
The thin-film electrodes reported in Table 1 were prepared by thermal decomposition of mixed precursor solutions drop cast on titanium foils (99.6%, 2.0 cm x 1.5 cm) with water/acetone solution (v/v, 50/50) for 10 min, then other 10 min in ethanol, and finally dried under a nitrogen stream at ambient temperature.

Precursor salts solutions, all prepared at 0.1 mol·L^{-1}concentration, were obtained by dissolution of $Mn(NO_3)_2$ in ethyl alcohol, $RuCl_3$ in isopropylic alcohol, $Co(NO_3)_2$ in ethyl alcohol, $CuCl_2$ in methyl alcohol, $FeCl_3$ in ethyl alcohol (Sotgiu et al., 2017). The adopted percentage is reported in Table 1.

After deposition, the electrodes were heated at 400 °C for 10 min. The procedure was repeated three times, and after the last cycle, the electrode was annealed for 1 h at 400 °C.

Table 1: Composition and electrochemical data of the prepared electrodes

Electrode	Ru	Mn	Cu	Co	Fe	q* (mC)	$E_{1/2}$ (V)	ΔE (V)	E_0 (V)	I_0 ($\mu A \cdot cm^{-2}$)
E 1	67	33	-	-	-	26.4	0.271	0.117	-0.120	0.58
E 2	50	50	-	-	-	28.7	0.272	0.137	-0.130	0.39
E 3	50	-	50	-	-	26.7	0.271	0.126	-0.045	0.59
E 4	50	-	-	50	-	14.2	0.268	0.126	-0.120	0.22
E 5	50	-	-	-	50	5.30	0.250	0.109	-0.110	0.41
E 6	50	40	10	-	-	40.2	0.276	0.141	-0.094	0.59
E 7	50	25	25	-	-	41.7	0.271	0.115	-0.076	0.41
E 8	50	10	40	-	-	58.0	0.266	0.137	-0.280	0.87
E 9	50	40	-	10	-	29.7	0.267	0.110	-0.026	0.51
E 10	50	25	-	25	-	29.7	0.267	0.130	-0.085	0.94
E 11	50	10	-	40	-	32.1	0.269	0.134	-0.068	0.97
E 12	50	40	-	-	10	64.2	0.270	0.165	-0.087	1.20
E 13	50	25	-	-	25	26.5	0.273	0.182	-0.028	0.22
E 14	50	10	-	-	40	10.6	0.266	0.159	-0.110	1.45

2.3 Electrode characterization
The surface morphologies of the electrodes were examined with a scanning electron microscope (SEM, Zeiss Gemini SIGMA 300 FEG SEM (Jena, Germany).

Electrochemical measurements were performed with an Amel System 5000 in a three electrodes cell. Acquisition software was CorrWare version 3.5c Scribner, elaboration software was CorrView version 3.5c Scribner. The prepared electrodes were employed as working electrodes (exposed surface of 1 cm^2) using a platinum counter electrode and a saturated Ag/AgCl reference electrode.

Cyclic voltammograms (CVs) were recorded, at ambient temperature (22 ± 1 °C), in a degassed aqueous solution of Na$_2$SO$_4$ (0.5 mol·L^{-1}) at scan rates of 10, 50, 100, and 200 mV·s^{-1}

To quantitatively evaluate the charge storage capacity, the voltammetric charge (q*) was determined by graphical integration of the voltammograms (second scan) recorded at 10 mV·s^{-1} in the potential window from 0.0 to 1.0 V, using Eq(1).

$$q^* = \frac{1}{\nu} \int_{V_1}^{V_2} i\,dV \qquad\qquad (1)$$

where:
q* = voltammetric charge
ν = scan rate (V s^{-1})
V_1 and V_2 are initial and final potential respectively (Volt)
i = current density (A cm^{-2})

CVs of the Fe(CN)$_6^{3-/4-}$ redox couple were also recorded in the same conditions, using 1·10^{-2} mol·L^{-1} of both K$_3$Fe(CN)$_6$ and 1·10^{-2} mol·L^{-1} of K$_4$Fe(CN)$_6$ at the same scan rates.

Polarization curves were performed, at ambient temperature (22 ± 1 °C), in a degassed aqueous solution of Na$_2$SO$_4$ (0.5 mol·L^{-1}) at a scan rate of 0.1 mV·s^{-1} vs open circuit potential (OCP) in the potential range from - 30 mV to 30 mV.

Accelerated life-time tests were conducted under galvanostatic conditions at a current density value of 4000 A·m^{-2} in a three-electrode cell consisting of the prepared electrode, a Platinum cathode of the same surface (1 cm^2), and a commercial Ag/AgCl electrode as the reference. The electrolyte was H$_2$SO$_4$ 0.5 mol·L^{-1}. During the test the temperature and agitation were kept constant at values, respectively, of 28±0.5 °C and 500 rpm. The electrode time-to-failure was estimated by the achievement of a potential of 7 V.

3. Results

The SEM images revealed that at low concentrations, all the films exhibited good surface homogeneity. The inhomogeneity effects, mainly consisting of the formation of aggregates and bubbles, were more evident with increasing concentration of the third element. In particular, at the maximum concentration, Copper (sample E 8 in Figure 1a) showed filamentous dendritic structures while Iron (sample E 14 in Figure 1c) exhibited a highly irregular-shaped morphology. The inhomogeneous dispersion could be indicative of a poor mutual solubility with segregation phenomena that are strongly conditioned by the variation of the reciprocal concentrations of the precursor salts. Samples containing Cobalt, on the other hand, displayed fewer defects even at high concentrations (sample E 11 in Figure 1b).
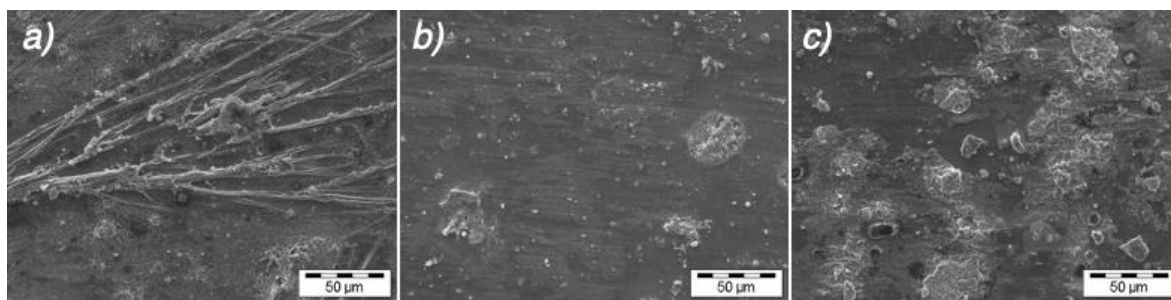

Figure 1: SEM images of E 8 (a) E 11 (b) and E 14 (c). Magnification: 500x

Figure 2a shows the voltammetric charge of the ternary films with the increasing nominal percentage of the third component. The charge was calculated according to Eq(1).

The values showed very characteristic trends depending on the nature of the third element. In particular, Cobalt unaffected the voltammetric charge value in a wide range of concentrations. The comparability of its charge values to those shown by the electrode containing only Ru and Mn (E 2) seems to indicate a substantial similarity in terms of charge storage between Co and Mn, under the adopted conditions.

On the contrary, Cu exhibited a slight improvement as the concentration increased, while Fe was always deleterious probably due to the aforementioned poor morphological uniformity of the deposit.

Figure 2b shows the voltammograms exclusively of the binary electrodes in the presence of a ferrocyanide/ferricyanide redox couple. All the analyzed films displayed the typical quasi-reversible shape even if the current peak of the Cu electrode was significantly higher than the others thus indicating a faster electron transfer kinetics. The overlapping curves of Mn and Co electrodes confirmed the already highlighted analogy in the electrochemical response of these two elements, under the adopted conditions.

The thermodynamic reversibility of the films was evaluated with the use of two parameters: the formal potential ($E_{1/2}$, Figure 2c), which corresponds to the half sum of the anodic and cathodic potentials, and ΔE (Figure 2d), which represents the difference between the anodic and cathodic peaks and in a reversible system at 25 °C corresponds to 59/n mV where n represents the number of exchanged electrons.

The values of the formal potential were distributed in a fairly narrow range of a few mV. The only clear trend is that of Copper which, as the concentration increases, decreases the formal potential by improving the performance of the electrode in terms of reversibility of the exchange between the redox couple in solution and the electrode surface.

A more significant effect was instead observed for ΔE. It is worth noticing that Iron alone with ruthenium presented values very close to what expected thus suggesting that the segregation and inhomogeneity of the deposit are evident only in co-presence with Manganese. Furthermore, the results indicated that the best performance was attributable to the Cobalt-based electrodes and the intermediate Copper sample.
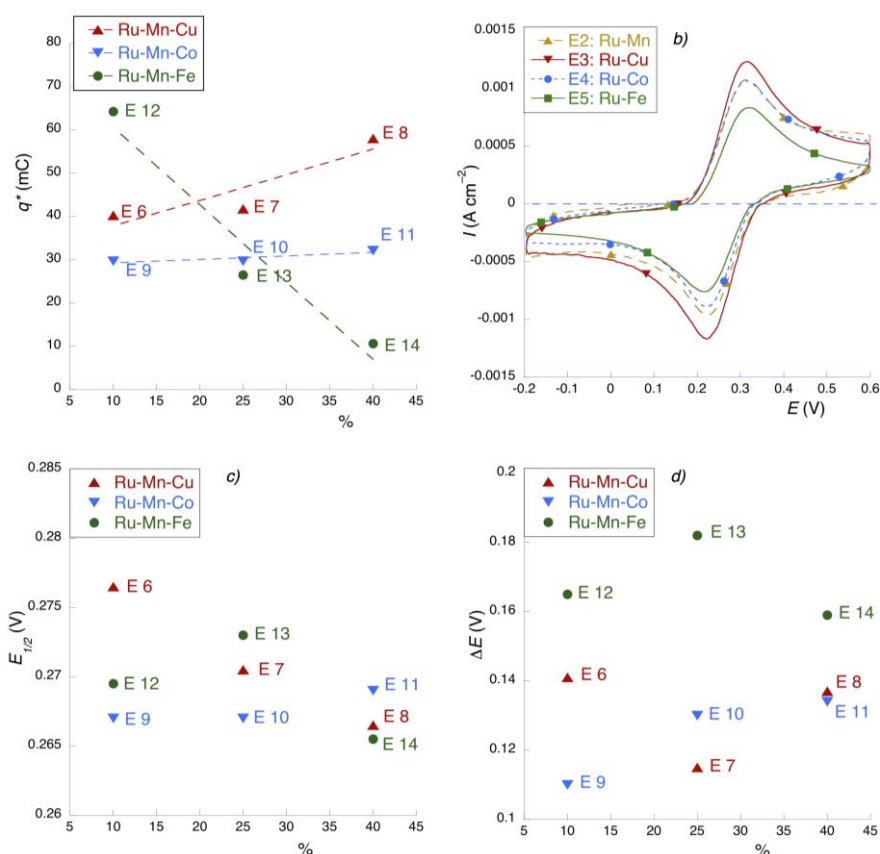

Figure 2: (a) Effect of the third element nominal percentage on voltammetric charge recorded at 10 mV·s⁻¹ in the range 0.0-1.0 V in Na_2SO_4=0.5 M; (b) Cyclic voltammograms for binary films in the presence of the $Fe(CN)_6^{3-/4-}$ couple; (c) Formal electrode potential measured (d) Anodic-to-cathodic peak separation. Conditions for b), c) and d) are: 0.01 M $Fe(CN)_6^{3-/4-}$, 50 mV·s⁻¹.

Potentiodynamic polarization studies of the binary and ternary mixed electrodes (Figures 3a and 3b) were performed to gain information about the polarization domains in a neutral aqueous solution. All samples were

immersed in the electrolyte for an adequate time to ensure stabilization of OCP before all experiments. The kinetic parameters are reported in Table 1. The I_0 and E_0 values ranged from 0.22 to 1.45 µA·cm^{-2} and from -0.280 to -0.026 V respectively. The almost corresponding potential of the binary mixed oxide samples E 2, E 4, and E 5 suggested very similar corrosion susceptibility. The presence of Copper oxide (E 3) shifted the potential to much less negative values, denoting a better response to corrosion processes.

As regards the ternary oxide electrodes (Figure 3b), the E_0 values varied in a fairly wide range of about 100 mV; this highlighted not only a different response depending on the type of metal combined with ruthenium and Manganese, but also a dependence on the relative ratio between Manganese and the third metal, while the ruthenium content remained constant. With Copper, the potential increased with the Cu/Mn ratio, probably due to the greater nobility of the Cu vs Mn. The increase in the Co/Mn ratio did not cause a similar behavior but rather a lowering of the value of E_0 was observed. With Iron, the presence of an excess of either Fe or Mn degraded the performance of the film, probably due to the inhomogeneous mixing of the two oxides.
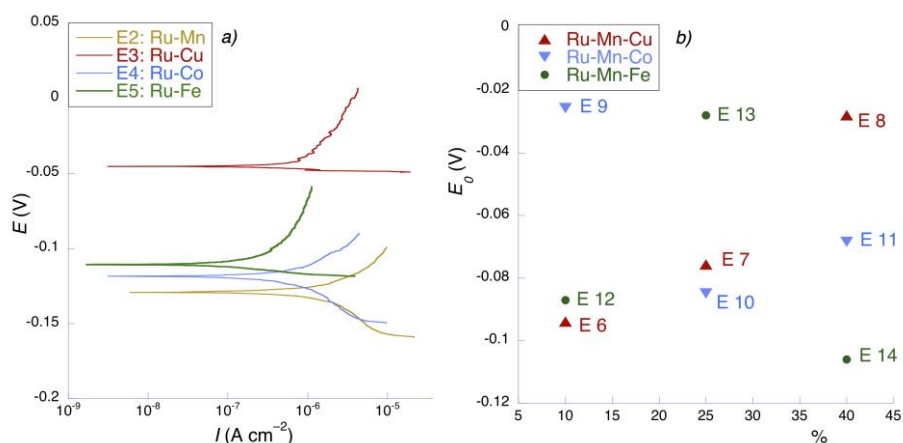

Figure 3: Potentiodynamic polarization curves for binary electrodes (a); Effect of the third element nominal percentage on the Corrosion Potential, E_0 (b). Conditions: Na$_2$SO$_4$=0.5 M, v=0.1 mV·s^{-1}.
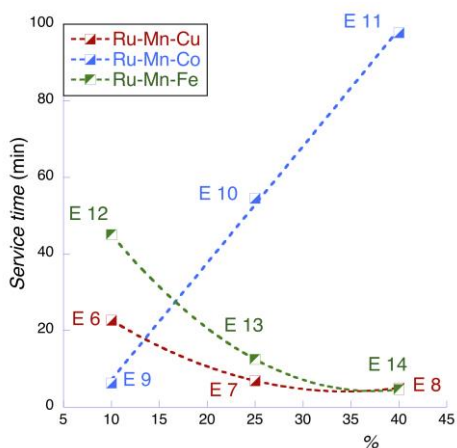

Figure 4: Effect of the composition on the stability of the electrodes expressed as the time required to reach the potential of 7 V. Conditions: Sel 1 cm^2; Ref. Ag/AgCl; j= 4000 A·m^{-2}; V = 50 ml H$_2$SO$_4$ 0.5 M, T=28±0.5 °C; mix = 500 rpm

The mechanical and electrical stability of the materials was measured through accelerated aging tests in sulfuric acid at high current density values (4000 A·m^{-2}). Figure 4 shows that only a few electrodes survived for a significant lifetime under such harsh conditions. In particular, the durability of the material benefited from the presence of Cobalt when its content equaled at least that of Manganese (E 10). When Cobalt was present at 40% (E 11) the electrode showed a more than a twofold lifetime than that of Iron at 10% (E 12) which represented

the best of those without Cobalt. On the contrary, increasing concentrations of Iron and Copper significantly worsened the durability of the materials as could be expected considering the uneven morphologies of these films.

Chen et al. (2011) reported a formula, Eq(2), correlating the lifetime values found in the accelerated tests conducted in seawater, SL_{AT}, with those that could be obtained under the milder operating conditions normally adopted, SL_{MC}, by knowing the corresponding current values and assuming for n a value in the range 1.4-2:

$$SL_{AT} = SL_{MC} \left(\frac{i_{MC}}{i_{AT}}\right)^n \tag{2}$$

Even with the limitations deriving from the fact that our electrolyte was different from seawater which was corrosive but certainly not acidic, this formula allowed an indicative estimate of the lifetime values. In particular, by considering for n the average value of 1.7, we can predict that the best performing electrode (E11) could work steadily for about 200 h at 200 $A \cdot m^{-2}$ or 130 h at 300 $A \cdot m^{-2}$. These data represented a very promising result also considering that the electrode surfaces had not undergone any significant modification to increase the adhesion of the coating.

4. Conclusions

Binary and ternary mixed-oxide thin-film electrodes were prepared and characterized.

Thin films including iron presented uneven deposits, very limited durability, and in general worse electrochemical performances. The poor solubility with Manganese hindered their co-deposition.

All electrodes showed a good faradaic response in the presence of a redox couple, with a quasi-reversible response. The potentiodynamic behavior was affected by the relative ratio of the metals used for the coating. In particular, a better response to corrosion processes as well as higher voltammetric charge was observed with increasing Copper content.

The electrode durability was negatively influenced by the increasing addition of either Copper or Iron and greatly improved by the addition of Cobalt.

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