

Heterogeneous Electron-Transfer Rate Constants for $\text{Fe}(\text{H}_2\text{O})_6^{3+/2+}$ at Metal Oxide Electrodes[†]

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Received: January 7, 2004; In Final Form: February 12, 2004

The title redox couple, in noncoordinating perchlorate medium, has been used to probe the electrochemical behavior of different IrO_2 -based electrodes; pure oxide electrodes, as well as IrO_2 - SnO_2 mixtures, have been investigated. The obtained results show that the electrode material strongly affects the electrochemical response. A tentative explanation, based on the different point of zero charge of the considered oxides, is presented.

Introduction

The characterization of different electrode materials, through the investigation of the behavior of a model redox couple, is common practice in electrochemistry. The redox equilibria of the main redox couples of iron, in aqueous solution, are among the most used for these purposes (see ref 1 and references therein). Particular care is however required in choosing the proper experimental conditions,^{1–4} avoiding the presence of ions (especially anions) that can alter the results. For the specific case of the iron(III)/iron(II) redox system, some authors have pointed out the role of, e.g., chlorides^{5,6} and sulfates^{7,8} in enhancing the electrode kinetics; accordingly, more reasonable results should be attainable by working in perchloric acid medium, as suggested by some authors,^{9–14} as well as by the present laboratory.^{1,4}

As far as the electrode material is concerned, an analysis of the literature has shown that the title redox couple has been appropriately (in some cases, traces of sulfates or chlorides were yet unfortunately present in solution) investigated only at noble-metal electrodes^{5–9,12–14} and at carbonaceous materials, i.e., glassy carbon^{11,15} and boron-doped diamond.^{1,4,10} Unfortunately, the few available data on metal oxide electrodes suffer from the choice of a sulfuric or hydrochloric acid medium,^{16–21} which hindered the properties of the electrode material as a result of the catalytic/complexing role exerted by the two anions.

Experimental Section

Titanium-supported, mixed-oxide electrodes of variable composition were synthesized by the usual thermal decomposition of precursor solutions.²² 2-Propanolic mixtures of $\text{H}_2\text{IrCl}_6 \cdot x\text{H}_2\text{O}$ (MaTecK) and a homemade, aquoorganic complex of tin(IV) were prepared to obtain the following IrO_2 nominal contents in the growing film: 5%, 10%, 20%, 30%, 35%, 40%, 50%, 60%, 70%, 100%. The various salt solution compositions were painted on both sides of sandblasted titanium plate substrates, evaporating the solvent at 120 °C for 5 min, and then pyrolyzing in air at 450 °C for 15 min. This procedure was repeated at least six times, until a thickness of about 1 μm was obtained; the

geometric surface area of the specimens was between 4.4 and 5.2 cm^2 . For the sake of comparison, titanium-supported, pure RuO_2 electrodes were also prepared, through the thermal decomposition of a 2-propanolic RuCl_3 solution.

Electrochemical investigations were carried out in a conventional three-electrode cell, housing the noble-metal, oxide-based electrode in a cylindrical platinum grid counter electrode; a double-walled, saturated calomel electrode (SCE), with an intermediate saturated NaNO_3 solution, was used as the reference electrode.

Initial cyclic voltammetries were obtained in 1 M HClO_4 (Fluka) pure supporting electrolyte; afterward, the same medium was considered for the investigations in the presence of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple. All solutions were prepared using MilliQ water ($\rho > 18 \text{ M}\Omega \cdot \text{cm}$) and analytical grade reagents; $\text{Fe}(\text{ClO}_4)_2$ and $\text{Fe}(\text{ClO}_4)_3$ (chloride $< 0.005\%$) hydrated salts were supplied by Aldrich and used without further purification.

The investigation of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ kinetics was carried out at room temperature, through measurements in a 5 mM solution containing both the reduced and the oxidized forms of the redox couple. Details on CV investigations and on the obtainment of quasi-steady polarization curves have been given in previous works.^{1,4}

Results and Discussion

The cyclic voltammetric curve, recorded at 10 mV/s at the pure (100%) IrO_2 electrode, in the presence of the title redox couple, is reported in Figure 1. Two well-defined, reversible peaks could be recorded, related to the oxidation of iron(II) to iron(III) in the anodic sweep and to the opposite reaction in the cathodic one. Analogous data, at the electrodes with 35 and 70 mol % IrO_2 , are reported in Figure 2; interestingly, higher voltammetric charges, compared to the data in Figure 1, have been measured for electrodes having an IrO_2 nominal content lower than 100%. Notwithstanding the different media, the present effect of composition on the voltammetric charge is in substantial agreement with the data previously reported by Trasatti and De Pauli²³ for CV data in 0.5 M H_2SO_4 .

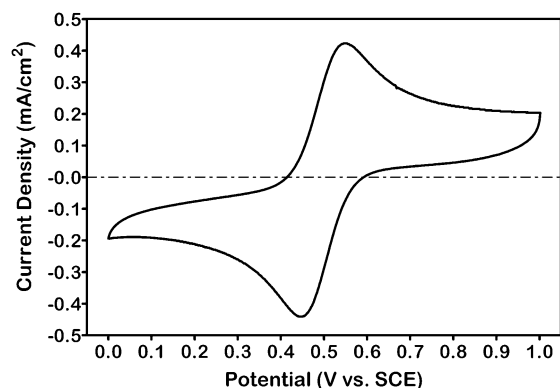
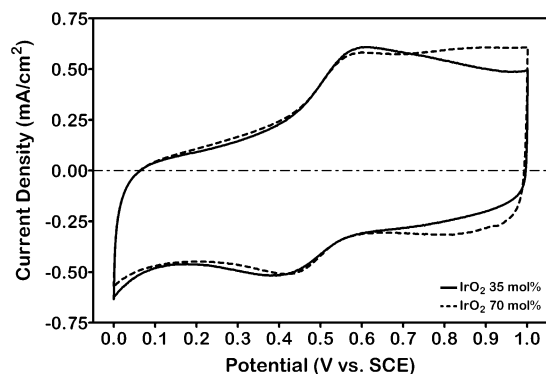
As anticipated in the Experimental Section, the behavior of IrO_2 and of the different IrO_2 - SnO_2 mixed-oxide anodes have been compared with that of pure (100%) RuO_2 electrodes, which have been prepared with different thicknesses, to verify a possible role of different electrochemically active areas, due to material porosity. CV data, recorded at 10 mV/s, at electrodes

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[†] This paper is dedicated to Prof. Gaetano Lodi, on occasion of his retirement. We gratefully acknowledge his valuable theoretical and practical contributions.

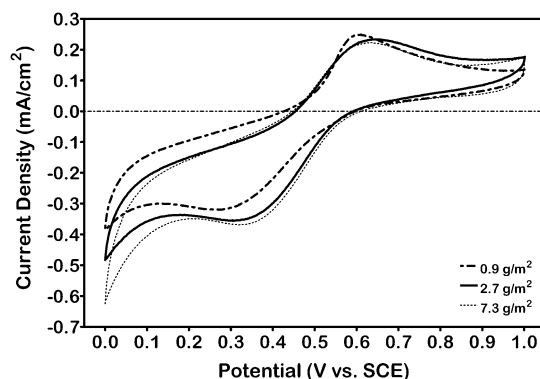
TABLE 1: Kinetic Parameters for the Fe^{3+/2+} Redox Couple at the Pure Noble-Metal Oxides Considered in This Work and Comparison with Literature Data

electrode material	PZC	j_0 (mA/cm ²)	k_{app}^0 (cm/s)	ref
100% IrO ₂	1.8 ²⁶	0.176	$(3.65 \pm 0.04) \times 10^{-4}$	this work
RuO ₂ (0.9 g/m ²)	3.88 ²⁷	0.0265	5.49×10^{-5}	} this work
RuO ₂ (2.7 g/m ²)		0.0435	9.01×10^{-5}	
RuO ₂ (7.3 g/m ²)		0.0457	9.47×10^{-5}	
thermally treated BDD	see the text		$(2.40 \pm 0.07) \times 10^{-5}$	1
as-prepared BDD	see the text		$(1.0 \pm 0.1) \times 10^{-5}$	1
rf-sputtered RuO ₂	≥ 5		9.60×10^{-6}	24
oxidized BDD	see the text		$(6.0 \pm 2.0) \times 10^{-6}$	1
fluorinated BDD	see the text		$(5.4 \pm 0.4) \times 10^{-7}$	4

**Figure 1.** Cyclic voltammogram for 5 mM Fe^{3+/2+} in 1 M HClO₄, recorded at the pure IrO₂ electrode (scan rate 10 mV/s, room temperature).**Figure 2.** Cyclic voltammograms for 5 mM Fe^{3+/2+} in 1 M HClO₄, recorded at two mixed-oxide electrodes, having a nominal IrO₂ content of 35 (solid line) and 70 (dotted line) mol % (scan rate 10 mV/s, room temperature).

having different RuO₂ loadings (0.9, 2.7, and 7.3 g/m², respectively), are reported in Figure 3. The behavior of the electrode with the lowest loading is somewhat different from that of the other two, for which the different thickness of the noble-metal oxide layer does not cause further changes in the kinetics of the redox couple under investigation, at least as a first approximation. Accordingly, current values have been normalized to the geometric electrode area.

For the obtainment of the apparent electron-transfer rate constants, quasi-steady polarization curves have been carried out at the different electrode materials, j_0 (and k_{app}^0) being related to the slope of the j vs η plots (low-overpotential approximation). Data for pure IrO₂ and RuO₂ electrodes have been collected in Table 1, in terms of exchange current density as well as k_{app}^0 values, together with some reliable results previously obtained at other electrode materials, which have been added for comparison. Although the title redox couple, in noncoordinating perchlorate medium, is considered an outer-sphere redox system,¹³ the electrode composition appears to significantly

**Figure 3.** Cyclic voltammograms for 5 mM Fe^{3+/2+} in 1 M HClO₄, recorded at three pure RuO₂ electrodes, having a nominal noble-metal loading of 0.9 (broken line), 2.7 (solid line), and 7.3 (dotted line) g of Ru/m² (scan rate 10 mV/s, room temperature).

modify the Fe^{3+/2+} kinetics, the highest electron-transfer rate constant being measured at the IrO₂ electrode, while slower rates have been observed at rf-sputtered RuO₂ and at samples of conducting diamond, which will be further discussed in the following.

Concerning the different RuO₂ electrodes, the kinetic data confirm the observations previously made on the basis of the CV curves, the behavior of the specimen with the lowest loading being somewhat different from that of the other two (which, in turn, show a kinetics practically unaffected by the oxide film thickness).

On the basis of the observed influence of the nature of the oxide film electrode and, to some extent, of its preparative path on k_{app}^0 , the latter has been tentatively correlated with the most relevant feature of an oxide surface, i.e., the ionogenic character of its dangling bonds, as expressed for instance by its point of zero charge (PZC; see, for example, ref 25). Data for RuO₂, IrO₂, and SnO₂ have been taken from a review by Ardizzone and Trasatti.²⁶ Among the just mentioned oxides, IrO₂ has the lowest PZC: a value of 1.8 has been reported by Trasatti;²⁷ for SnO₂, a value of about 4.7 has been used in ref 26. Concerning RuO₂, differences exist among materials prepared in different ways: in general, “hydrated” RuO₂ has a lower PZC, compared to more dry specimens (such as those obtained at a high calcination temperature); in consideration of the method of preparation of the RuO₂ electrodes adopted in the present work, a PZC value of 3.88 (as suggested by Goodenough et al.²⁸) was chosen. On the other hand, a less acidic PZC value (≥ 5) should be assigned to the specimens synthesized by rf-sputtering.

Accepting the above listed PZC values, the results of the present investigation seem to point toward a dependence of the Fe^{3+/2+} kinetics on the PZC, higher k_{app}^0 values being measurable at more acidic oxides. In this context, boron-doped diamond could be inserted because of some very recent results on the surface characterization of samples subjected to different

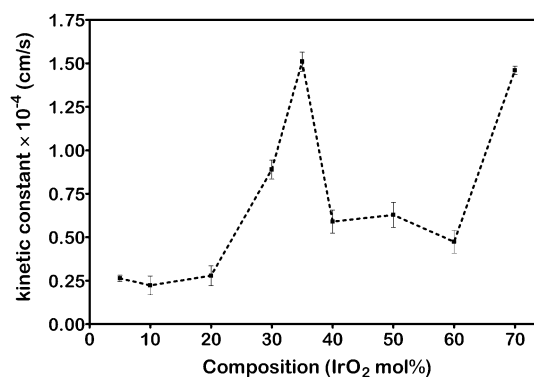
TABLE 2: Kinetic Parameters for the $\text{Fe}^{3+/2+}$ Redox Couple at the Various Mixed-Oxide Electrodes Considered in This Work

electrode composition	slope ($\text{d}/\text{d}\eta$)	j_0 (mA/cm^2)	k_{app}^0 (cm/s)
100% IrO_2	6.864	0.176	$(3.65 \pm 0.04) \times 10^{-4}$
70% IrO_2 –30% SnO_2	2.74	0.0703	$(1.46 \pm 0.02) \times 10^{-4}$
60% IrO_2 –40% SnO_2	0.8909	0.0229	$(4.74 \pm 0.66) \times 10^{-5}$
50% IrO_2 –50% SnO_2	1.18	0.0303	$(6.28 \pm 0.72) \times 10^{-5}$
40% IrO_2 –60% SnO_2	1.109	0.0285	$(5.90 \pm 0.67) \times 10^{-5}$
35% IrO_2 –65% SnO_2	2.831	0.0726	$(1.51 \pm 0.55) \times 10^{-4}$
30% IrO_2 –70% SnO_2	1.672	0.0429	$(8.89 \pm 0.55) \times 10^{-5}$
20% IrO_2 –80% SnO_2	0.5244	0.0135	$(2.79 \pm 0.57) \times 10^{-5}$
10% IrO_2 –90% SnO_2	0.4198	0.0108	$(2.23 \pm 0.54) \times 10^{-5}$
5% IrO_2 –95% SnO_2	0.4967	0.0127	$(2.64 \pm 0.18) \times 10^{-5}$

oxidative treatments;²⁹ in particular, specimens thermally oxidized, at 400 °C for 30 min at room atmosphere, have shown a significant surface enrichment in silicon (the substrate-constituting element), which was further transformed into SiO_2 . Considering that the PZC of silica is ~ 2 , and the thermally treated diamond electrode showed a surface silica content of about 36.5 mol %, ²⁹ the position of this electrode material in Table 1, between the two considered types of RuO_2 (i.e., between materials for which PZC values of ~ 3.88 and ≥ 5 have been proposed), is not surprising. The position of the other BDD samples could be difficult to explain, if only the PZC of these different materials is considered; however, the explanation already given in ref 4 does not seem to contrast with the present attempts. In fact, changes in the hydrophobic/hydrophilic character of the different BDD specimens may be reflected in the solvent structure at the electrode/solution interface, paralleling the modifications in surface oxide acidity (PZC), but with less pronounced consequences.

To check the validity of the above correlation, a set of IrO_2 – SnO_2 mixed-oxide electrodes have also been investigated, and pertaining results are reported in Table 2. A thorough examination of these data would necessarily require consideration of the detailed composition of the different samples; for electrode materials nominally similar to the present ones, Trasatti and De Pauli reported a surface enrichment of iridium,²³ while Balko and Nguyen gave an account for the opposite phenomenon, i.e., a surface depletion of Ir.³⁰ In the absence of the surface composition of the present mixed-oxide electrodes, we decided to assume a substantial homogeneity through the oxide film, hypothesizing a surface composition not different from the nominal one. Accordingly, the general trend of the k_{app}^0 values in Table 2 indicates that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ kinetics decreases with the IrO_2 content in the mixed-oxide films, in agreement with the PZC-based explanation previously proposed. On the other hand, a more careful analysis points to a significant increase of k_{app}^0 for iridium contents between 30 and 40 mol %, as shown in Figure 4; the maximum value, obtained for an IrO_2 content equal to 35 mol %, is higher than that recorded at the mixed oxide with 70 mol % IrO_2 and about half the rate constant obtained at the pure IrO_2 electrode. Since mixed oxides could have a PZC nonlinearly correlated to those of the pure components, due to the occurrence of synergetic effects,³¹ some discrepancies may arise, especially in the presence of solid solutions, which is probably the case for compositions with an IrO_2 content between 20 and 40 mol %.

As far as the different RuO_2 -based electrodes are concerned, at the sample with the lowest loading (0.9 g of Ru/m^2), a slower $\text{Fe}^{3+/2+}$ kinetics was observed; given that the electrode was prepared by a unique brushing procedure, a segregation of Ti from the support or the obtainment of only a partial coverage

**Figure 4.** Dependence of the $\text{Fe}^{3+/2+}$ apparent electron-transfer rate constant on the IrO_2 content in the considered mixed-oxide electrodes. Data were obtained at room temperature.

of the titanium plate cannot be excluded. In both cases, the catalytic layer would be composed of RuO_2 , TiO_2 , and, probably, a solid solution of them. Apart from the specific surface structure of the electrode, the PZC of titania has been reported to lie around 6, with values between 5.5 and 6.2,²⁶ and thus, the low k_{app}^0 might reflect the mixed-oxide character of the RuO_2 specimen.

Conclusions

The obtained results have shown that, despite the outer-sphere character of the investigated redox system,¹³ the electrode material has a major role in determining the electron-transfer rate. In particular, a k_{app}^0 value of 3.65×10^{-4} cm/s could be measured at the pure IrO_2 electrode, i.e., a kinetics 1 and 2 orders of magnitude faster than that observed at polycrystalline Au and Pt, respectively.^{7,12} Again, changes in solvent structure at the electrode/electrolyte interface could be the reason for the observed dependence of the kinetics of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple;⁴ in addition, dealing with oxide electrodes, a tentative explanation could be based on the PZC of the different electrode material. Further research is in progress in our laboratories on the characterization of noble-metal-based anodes suitable for oxygen evolution.

Acknowledgment. The authors are grateful to Tiziano Crosara for his precious help in the preparation of the different samples used in this work, and to Loretta Andrich for carrying out part of the experiments, in the frame of a stage supported by the Amministrazione Provinciale di Belluno (Italy).

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