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Post-discharge plasma-chemical oxidation of Iron(II) complexes

A. DOUBLA[1,3], F. ABDELMALEK[2], K. KHÉLIFA[2], A. ADDOU[2] and J.L. BRISSET[3]
[1]*Inorganic Chemistry Laboratory, University of Yaounde-I, Cameroon*
[2]*STEVA Laboratory, University of Mostaganem, Algeria*
[3]*Laboratoire d'Electrochimie (LEICA), University of Rouen, France*

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Abstract

The plasmachemical properties of an electric discharge in humid air are considered by examining the oxidation of Fe(II) to Fe(III) aquo-ions in a solution exposed to the discharge. The reaction product is characterised and quantified by means of the thiocyanate complex $FeSCN^{2+}$. The reaction mechanism shows two distinct steps: a rapid step directly depending on the treatment time and a slow post-discharge step, which are both ascribed to species formed in the discharge (i.e., respectively to OH radical and to hydrogen peroxide or nitrate ions). These concerned species are able to react either at the liquid surface (OH) or to diffuse into the solution and react as solutes. Experimental arguments in favour of zero and first order reaction steps are given. A particular reactor design involving a multibladed electrode is tested at the juncture and its use considered for further industrial applications.

1. Introduction

Preliminary experiments relevant to plasma oxidation of solutions at atmospheric pressure showed that Iron materials involved in the reactor device were sensitive to corrosion when the plasma was produced by a gliding arc discharge in humid air, so that the metal parts had to be replaced by less cheap stainless steel items. A more detailed investigation [1] showed that even stainless steel was affected by long plasma treatments. Owing to the fact that rusty coatings often result from the exposure of iron materials to an air plasma, we investigated oxidation of Fe(II) solutes, as a step in the general mechanism for the plasma corrosion of iron. This paper deals with the oxidation of Fe(II) species dispersed in aqueous solutions and exposed to a humid air plasma of the gliding arc type.

1.1. *Gliding arc ('Glidarc') discharge*

The gliding arc device was suggested by Czernichowski et al. [2, 3] and later examined as a convenient source of quenched nonthermal plasma in several laboratories, mainly for pollution abatement of gases. The glidarc treatment of liquids was considered in a more limited number of research groups [4, 5] and especially developed in our laboratories.

When two diverging conductors disposed in humid air and distant by few millimetres are raised to a convenient potential difference (i.e., several kV), an electric arc forms at the shortest electrode gap, and presents the character of a thermal plasma: the electrons and the heavy species (i.e., molecules, ions and atoms) have close energies, which means that a local thermodynamic equilibrium is established. A gas flow placed along the reactor axis, gently pushes the feet of the arc along the electrodes, so that the arc length increases until the arc is short-circuited by a new one and breaks into a plume. The energy of the heavy species then lowers, as does the macroscopic temperature, and a quenched plasma at quasi-ambient temperature and atmospheric pressure results in the plasma plume. Aqueous solutions can thus be exposed to such a plasma, and the liquid target is subjected to the chemical properties of the impinging activated species of the plasma.

1.2. *Chemical properties*

The chemical properties of the species formed in a gliding arc plasma in humid air were investigated on solid and liquid [6–10] targets. The major reactions observed in an aqueous target are pH lowering and strong oxidising effects, which are interpreted as direct consequences of the formation of NO and OH radicals. These radicals were identified in the discharge and quantified by emission spectrometry [7, 8]. NO leads to the formation of NO_2, nitrite and nitrate ions as stable species, which are thus associated with acid changes [6]. However the high standard potentials of the HNO_2/NO and NO_3^-/HNO_2 systems (i.e., 1.00 and 1.04 V vs NHE, respectively) explain the oxidizing character of the nitrate ion. The OH radical is one of the most powerful oxidizing agents (i.e., $E°(OH/H_2O) = 2.85$ V vs NHE) and responsible for oxidation reactions, both by its own properties and by its derivative and/or parent molecule H_2O_2:

$$H_2O_2 = 2\,OH$$

The occurrence of hydrogen peroxide in the solution was confirmed by the formation of the characteristic Ti(IV) and V(V) complexes.

Oxidation of inorganic and organic aqueous solutes by means of a gliding arc treatment in ambient air has been reported for various reactor configurations: iodide leads to iodine and even to iodate [4, 6] and many organic compounds were degraded up to CO and CO_2 [9, 10]. Thus, the gliding arc technique is a promising method for pollution abatement both for gases and liquid effluents.

Plasma oxidation of Mohr salt was also examined [11]. This paper is devoted to post discharge phenomena observed on iron salts exposed to a gliding arc treatment in humid air.

1.3. *Reaction mechanism*

The general reaction mechanism between a plasma gas and a liquid target may be approached as follows, by considering that the reaction takes place at the gas–liquid interface. The active species of the plasma react at the liquid surface on impinging with condensed target molecules:

$$\text{Active oxidizing species}|_{\text{gas}} + \text{target molecule}|_{\text{liquid surface}} \rightarrow \text{oxidation product}|_{\text{solution}}$$

A more detailed mechanism cannot be given because it largely depends on the natures of the solute and the gas. However, the literature [12] provides radical mechanisms which can be invoked for gliding arc treatments of organic compounds. For example, the degradation of organic wastes involves a radical multistep mechanism, for example, hydrogen atom abstraction to yield peroxoradical, formation of an alcoxyradical resulting from NO attack, transposition, and resumption of the reaction cycle [13].

It is, however, experimentally known from numerous glidarc treatments of organic dyes, spent solvents or even industrial wastes that two limiting situations may be considered. For concentrated solutes, the target molecules present at the surface are much more numerous than the impinging species, so that a major part of the gas species are involved in the reaction, and their number directly depends on the energy provided to the discharge, for a given gas flow rate. Hence the number of transformed species in the solution is limited by the number of impinging species, so that the resulting mechanism is zero order in solute.

For low concentrated solutes (or towards the end of the treatment of a concentrated solute), the solute molecules are in low concentration at the surface. The reaction is then limited by the target species present at the liquid surface, which diffuse from the bulk liquid. The slow step is related to diffusion and an overall first order kinetic reaction is observed for the solute. This dual kinetic order was actually observed for several examples of plasma-treated liquid effluents [11].

2. Experimental details

The typical plasma reactor was described [1, 10, 11] as formed by two diverging conductors (the electrodes) raised to a suitable potential difference of around 10 kV for an electrode gap of a few millimetres. An arc forms at the electrode neck. It moves along the electrodes, as it is pushed by the gas flow along the axis of the electrodes. The arc gets longer before breaking into a plasma plume, and a new arc forming, so that the thermal plasma turns to a quenched nonthermal plasma. This plasma plume strokes the liquid surface, so that the reaction can take place at the gas–liquid interface.

For the present study, the device (Figure 1) was slightly modified by using a multibladed electrode and a plane electrode. The multi-bladed electrode consisted of a series of seven identical semi-elliptic blades of the same profile as for the basic device [10] and electrically connected in parallel. This electrode was positioned 4 mm in front of a plane electrode (Figure 1). The whole device was not placed in a reactor, but over a beaker containing the target solution.

The target solution was disposed normally to the axis of the reactor at a distance close to 40 mm. The solution was not stirred but homogenized by the vortex due to the impinging gas flow.

The selected feeding gas was water saturated air, provided by a compressor and passing through a bubbling flask before entering the reactor (gas flow rate 15 L min^{-1}).

The reagents were analytical grade chemicals purchased from Merck or Aldrich and used without further purification.

A volume of 500 mL of an equimolar (2.5 mM) mixture of Fe(II) and SCN^- was exposed to the humid air plasma for the treatment time t^* (min). After the discharge was switched off, a sample of the treated solution was examined spectrophotometrically and its absorbance measured at the absorption peak of the Fe(III)–SCN complex (i.e., at 450 nm).

3. Results and discussion

3.1. *Complex formation*

We focus in this paper on the changes occurred in the solution after the discharge is switched off, which will be

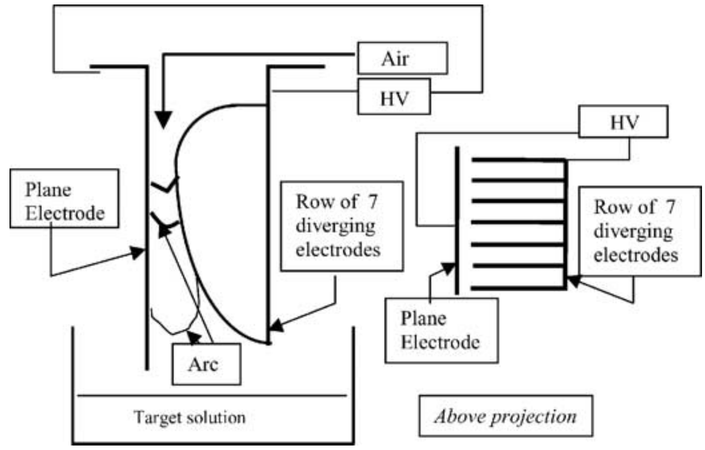

Fig. 1. Scheme of the experimental device used with the multibladed electrode and the plane electrode.

referred to as post-discharge phenomena, and we select as illustrative example that of Fe(II) complexes.

The colour of the plasma treated target solution got reddish, which suggested the formation of the Fe(III)–SCN complex. This feature is referred to as a discharge induced reaction and takes place before the post-discharge phenomena develop. Spectrophotometric measurements at the absorption peak of the Fe(III)–SCN complex (i.e., at 450 nm) were performed immediately after the discharge was switched off, and were thus 'zero' absorbance values with respect with the post discharge. These 'zero' values linearly increase with the relevant exposure time t^*_{exp} to the plasma at the beginning of the treatment and tend to a limit for long plasma treatments. This confirms that Fe(III) species reacts with thiocyanate ions to form the coloured complex at the beginning of the treatment. The reaction is a zero-order mechanism with the relevant kinetic constant 8.3×10^{-5} M s^{-1}.

These results confirm other experiments [11] performed with a more conventional glidarc device fitted with two single-bladed electrodes (kinetic constant: 3.4×10^{-4} M s^{-1}). The discrepancy between the values of the kinetic constants may be attributed to slightly different gas flow-rates, to the geometry of the reactor and to the use of a 'closed' reactor for which the exchanges with the ambient atmosphere are limited by a glass vessel [11].

3.2. *Post-discharge phenomena*

If the tested solutions, are left in post-discharge conditions without adding any extra energy (i.e., in the dark and at ambient temperature) after having been exposed to the plasma for t^*_{exp} (min), their absorbance A_{450} at 450 nm changes with time: A_{450} increases or decreases, depending on t^*_{exp}. This feature indicates that two reaction steps take place.

For moderate exposure times t^*_{exp} (i.e., for $t^*_{\text{exp}} <$ 30 min), the tested solution is a mixture of formed complex Fe(III)–SCN, excess SCN$^-$ ligand and Fe(II) ions. A_{450} increases (Figure 2) and tends to a limiting value, which shows that the coloured complex Fe(III)–SCN goes on forming out of the discharge. Since the time life of OH radicals is short and the complex formation is rapid, the overall process is controlled by the formation of Fe(III) which may result from the action of both OH and hydrogen peroxide on acid Fe(II) salt solutions.

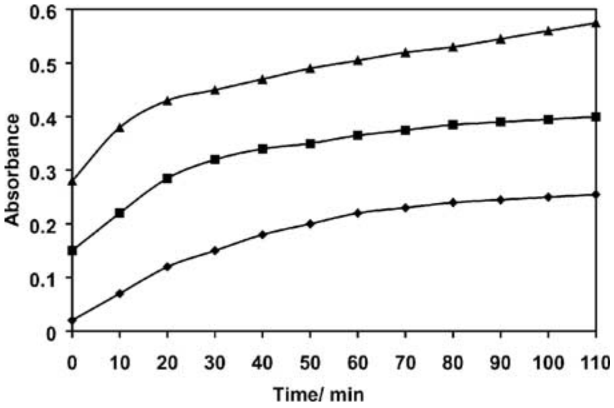

Fig. 2. Evolution of the absorbance against time relevant to post-discharge phenomena for moderate plasma treatments ($t^*_{\text{exp}} < 30$ min). Key: (◆) 3, (■) 7 and (▲) 10 min.

$$\mathrm{H_2O_2 + 2Fe(II) + 2H+ \rightarrow 2Fe^{3+} + 2H_2O}$$
$$E°(\mathrm{H_2O_2/H_2O}) = 1.78\,\mathrm{V\ vs\ NHE}$$

$$\mathrm{Fe^{3+} + SCN^- \rightarrow FeSCN^{2+}}$$

Plots of absorbance A_{450} against t are initially increasing straight lines, so that they reflect a zero order mechanism:

$$\frac{dA}{dt} = \frac{dC_{\text{FeSCN}}}{dt} = k$$

Additionally, the relevant slopes k are linearly correlated with the values of the absorbance A_{450} of the solution when the post-discharge process starts (i.e., the absorbance of the solution treated for an exposure time t^*_{exp} to the plasma), that is, to the concentration C_{FeSCN} of the FeSCN^{2+} complex formed by the discharge:

$$k = a\,C_{\text{FeSCN}} + b$$

$$k = 0.4 \times 10^{-3} A_{450} + 7 \times 10^{-5} \quad r^2 = 0.92$$

It can thus be concluded that oxidation of iron(II) obeys an overall first order law, if the constant b can be neglected to a first approximation. Diffusion of H_2O_2 in the aqueous phase explains this overall first order mechanism.

In addition, the A against t plots also tend to limiting values A_∞ at infinite time (Figure 2). These A_∞ values are reasonably linear ($r^2 = 0.99$) functions of the starting concentrations in complex C_{FeSCN} when the post-discharge begins: $A_\infty = \lambda C_{\text{FeSCN}}$. This feature means that the maximum concentration of complex depends on the treatment time t^*_{exp} by the plasma. It agrees with the assumption that the plasma treatment forms two kinds of reactive species: the first one rapidly reacts with the solute Fe(II) and the second less rapidly. The relevant species may be OH radicals and hydrogen peroxide, respectively.

For long exposure times t^*_{exp} (i.e., for $t^*_{\text{exp}} > 30$ min), the absorbances of the plasma treated solutions decrease in post-discharge conditions (Figure 3) and tend to steady values A_∞ at infinite time. This feature means that the concentration C_{FeSCN} of complex formed by the discharge (i.e., at the beginning of the post-discharge conditions) decreases during the post-discharge. The complex disappears and two relevant assumptions must then be considered to account for this feature:

(i) the complex dissociates, because the large acid effects induced in the solution by plasma treatment favour the formation of molecular thiocyanic acid, which is almost a strong acid ($\text{p}K_\text{a} \approx 0.8$). The pH lowering varies in the same way as the exposure time t^*_{exp} to the discharge and may therefore be important for long treatment.

$$\text{FeSCN} + \text{H}^+ \rightarrow \text{HSCN} + \text{Fe}^{3+}$$

According to this assumption, the decrease in the complex concentration in post discharge conditions may be attributed to pure chemical reactions.

(ii) the complex degrades, due to the oxidation of the ligand to sulphate and cyanate. Experiments confirm that the ligand concentration is little affected by the plasma treatment, and this feature agrees with the fact that oxidation of thiocyanate is known to be slow. The relevant assumption can thus be discarded.

Evolution of the A_∞ values relevant to short and long plasma treatments t_{exp} and measured three days after the discharge is switched off is shown in Figure 4, which thus illustrates the overall changes in the complex concentration at the end of the discharge and post-discharge reactions. The analysis of the set of A_∞ values confirms the occurrence of two kinetic models with zero and first order steps, respectively.

4. Additional discussion on the multibladed device

Additionally to the post-discharge phenomena, which have not yet been considered on the basis of plasma-chemical reactions, the results also lead us to examine the question of the device tested.

As mentioned, a new type of reactor with a new electrode arrangement involving a plane electrode and a multibladed electrode was investigated. Although one single electric arc is ordinary formed at each moment, two consecutive arcs may form between the plane electrode and two different blades, which diversifies and enlarges the contact area of the solution with the plasma. An increased number of solute molecules present at the surface are thus concerned with the flux of the impinging activated species. Thus, the new device

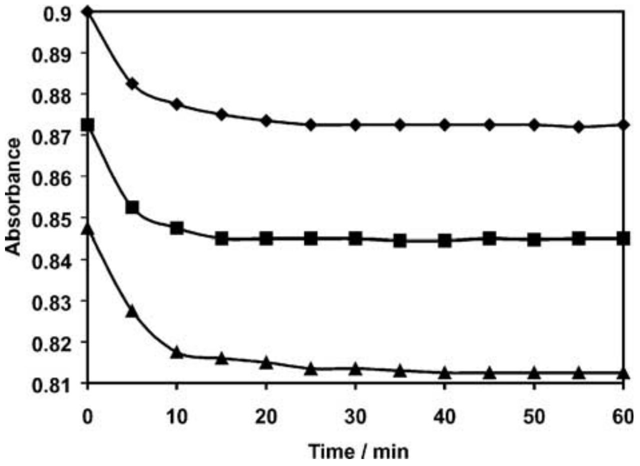

Fig. 3. Evolution of the absorbance against time in post-discharge conditions for long plasma treatments ($t^*_{\text{exp}} > 30$ min). Key: (◆) 60, (■) 50 and (▲) 40 min.

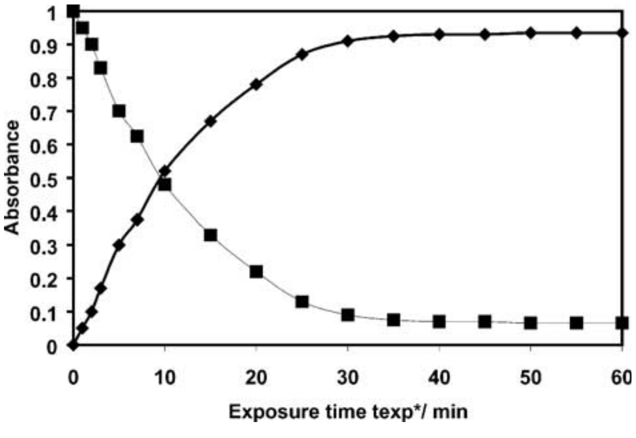

Fig. 4. A_∞ values resulting from the evolution of the absorbance A_{450} of the solution, measured three days after the discharge was switched off, as a function of the exposure time t^*_{exp} to the discharge. The Fe^{3+} plot is relevant to the formation of the oxidized complex FeSCN^{2+} while the complementary Fe^{2+} plot illustrates the decrease in the reduced iron concentration. Key: (◆) Fe^{3+} and (■) Fe^{2+}.

is superior to the former one involving two single electrodes.

If by chance, several arcs form simultaneously and involve different blades, the current intensity of the discharge will be reduced accordingly, as will be the number of activated species formed in the discharge. The chemical efficiency of the plasma treatment should thus be reduced. However, the area concerned by the impinging species is different for each arc, so that post-discharge phenomena may take place in the target solution, prevent the liquid surface from being passivated by reaction products and balance the reduced flux of activated impinging species.

The thermal effect on the multibladed electrode is also limited, since each blade may dissipate heat more easily than the standard device. The lowered thermal radiation has a minimized effect on the liquid target, which may be of major interest to prevent reaching the flash point of air–organic mixtures.

The benefit of using a multibladed electrode device remains limited in the case of the post discharge oxidation of iron(II), since the kinetic constants for the oxidation remain close for both types of electrode design. However it is preferred in cases of surface treatments requiring larger treated area.

5. Conclusions

Results on the plasma-chemical oxidation of Fe(II) complex dissolved in solution have provided interesting results from various points of view.

They allowed us to operate a new design of reactor involving one multibladed electrode which was operated in the same way as a more classical device [11]. We could thus rapidly compare the efficiency of the designs. Oxidation of Fe^{2+} target solution was observed with both reactors, and the overall oxidation rates were close in spite of slightly different working conditions. The example of the oxidation of Fe^{2+} was interesting for demonstrating the feasibility of using a multibladed electrode.

This new multibladed device allows a better use of the electric energy provided to the system than the classical device, since the active species are more widely dispersed at the target surface and may react at the solute either on impingement or according to a post discharge mechanism. In all cases, it lowers the residence time of the target in the plasma reactor, which is of obvious interest for industrial plasma treatments of solutes. In the case of surface treatment of solids, the dispersion leads to a more limited degradation and an enlarged treated area.

The second important point refers to the oxidation mechanism. Post-discharge phenomena occur in treated liquid targets. Thus the plasma treatment implies two steps: a rapid step on exposing the solution to the discharge and a slow post-discharge step, both of which concern species formed in the discharge. The rapid step may be attributed to the impinging OH radicals while hydrogen peroxide formed in the target solution is likely involved in the post-discharge reaction.

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