

Influence of Metal Ions on Oscillatory Behavior of Zinc Anode in Nitric Acid-Potassium Dichromate Media

F. Crisan^{a,*} and E. Sallo^b

^aCounty Lab for Pesticides Quality Control, Bodrogului Str., No. 3, 310059, Arad, Romania

^bChemistry Institute of Romanian Academy, Mihai Viteazul Bv., No. 24, 300223, Timisoara, Romania

(Received 18 September 2008, Accepted 20 February 2009)

A zinc anode in acidic media is a new oscillatory electrochemical system which manifests interesting behaviors, from steady states to simple oscillations and chaos. This paper presents an experimental study of the influence of metal ions on the shape, amplitude and duration of the cell potential oscillations, and gives a qualitative explanation of the system's behavior. A small quantity of Cu^{2+} , Zn^{2+} or Fe^{3+} ions added to the system change dramatically the potential oscillations from chaotic behavior to simple oscillations. The method may be used for chaos attenuation.

Keywords: Zinc, Nitric acid, Dichromate, Oscillations, Chaos, Metal ions

INTRODUCTION

Dynamic behavior of some metals at the transition region from the active state to the passive state, from steady state to simple, double or chaotic oscillations, affords a large area of research interest in corrosion and protection of metals as well as understanding the oscillatory phenomena which occur at the solid/liquid interface processes [1-16].

Self-organization of the electrochemical systems is not limited to temporal phenomena but could also involve spatial pattern formation [2,9,11,13]. Most frequently studied electrochemical system, from the point of view of the dynamic behavior, is iron anodization in sulfuric acid media [2,4,6,9]. Besides iron, there are many other metals which present current or potential oscillations (Ni, Cu, Co, Pb, Ag, Zn, alloys) in certain media (acid, alkaline or salts solutions). The behavior of zinc electrodes has been studied in alkaline solutions as cathode [14,15], but in the acidic media their

behavior is almost unknown [16,17].

Appearance of the oscillations is related to a precipitation-dissolution process of a chemical species (salt, oxide or hydroxide) at the electrode surface or chemical reactions that have an autocatalytic step [3,15]. For the anodic dissolution of iron, current oscillations are associated with mechanical oscillations of the electrolyte level [12] or with passive and active zones appearance at the electrode surface, depending upon working electrode-counter electrode distance [13]. The precipitation-dissolution mechanism is the most extensive mechanism, which tries to explain potential or current oscillations and seems to be the closest to the real phenomena.

It is well known that zinc, as well as certain other metals and alloys, show the phenomenon of metallic passivity. In other words, metal becomes inert under particular environmental conditions since its surface is covered by a thin oxide film. In a passive state, the defects of the protective film may induce propagating reaction zones, which lead to the dissolution of the passivity layer and turning the electrode into active state.

*Corresponding author. E-mail: florincrisan2000@yahoo.com

Potential or current oscillations of a zinc anode immersed in a nitric acid-potassium dichromate solution depend upon solution composition (acid or dichromate concentration), nitrate ions concentration (added as potassium nitrate solution), stirring and potential (for potentiometric measurements).

This work presents an experimental study of the dynamic behavior of a zinc anode in nitric acid media when small quantities of some metal ions are added to the system. If the system presents chaotic behavior in some experimental conditions, the complexity of the potential oscillations decreases dramatically when Cu^{2+} , Zn^{2+} and Fe^{3+} ions are added to the initial solution, leading to simple (one-period) oscillations, depending upon ions quantity. In some cases, oscillations cease to exist or turn into groups of simple oscillations connected by no oscillations zones.

EXPERIMENTAL

Experiments were carried out using an electrochemical cell with two electrodes, at room temperature. The working electrode was a zinc rod, Merck, 99.9% purity, with eight mm diameter, embedded in an insoluble muff, so that only the end

of the rod was exposed to the solution. Active surface of the electrode was around 50 mm^2 . Reference electrode was a platinum wire, one mm diameter.

The electrolyte was prepared from analytical grade reagents and purified Millipore water ($>18 \text{ M}\Omega \cdot \text{cm}$ resistivity). We used a potassium dichromate solution 0.4 M, prepared from potassium dichromate Riedel-deHaën 99.8% purity and nitric acid solution with 1 M concentration, prepared from nitric acid Fluka 65% purity. The initial solutions of the electrolyte for each determination were obtained by mixing potassium dichromate and nitric acid solutions described above. The working electrode was polished with 600 and 1000 grade emery paper, washed with water and wiped prior to each experiment. The potential oscillations were recorded using a Speedomax XL recorder, $4 \text{ M}\Omega$ internal resistances. A magnetic stirrer was used to stir the system.

We used 0.1 M solutions of each cation, obtained from Cu(II) , Zn(II) and Fe(III) hydrated sulfates.

RESULTS AND DISCUSSION

Figures 1, 2 and 3 represent the influence of the Cu^{2+} , Zn^{2+}

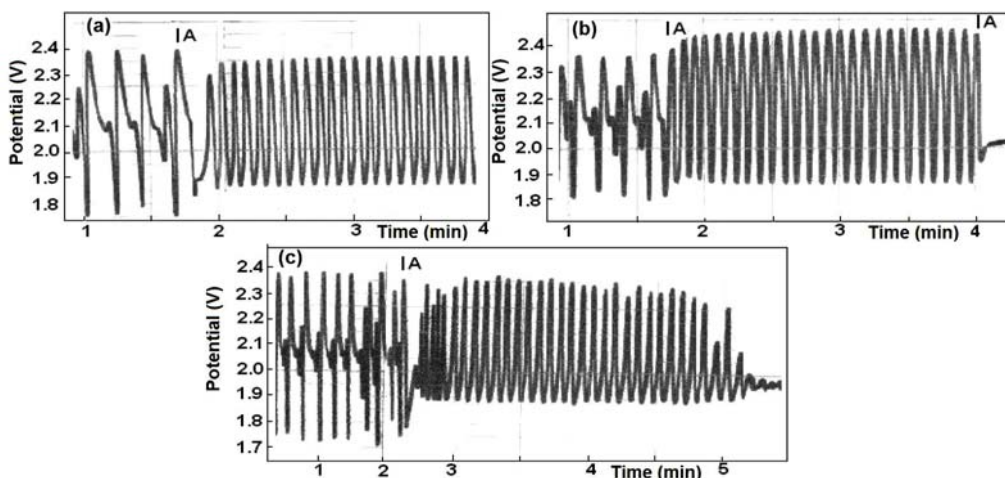


Fig. 1. Influence of Cu^{2+} ions on shape, amplitude and duration of the cell potential oscillations. In each case, initial solution contained a nitric acid:potassium dichromate molar ratio of 2.5 (50 ml nitric acid 1 M + 50 ml potassium dichromate 0.4 M). At the points marked with A, different volumes of a 0.1 M Cu^{2+} solution were added: (a) 0.4 ml, (b) 0.5 ml and (c) 0.7 ml.

Influence of Metal Ions on Oscillatory Behavior

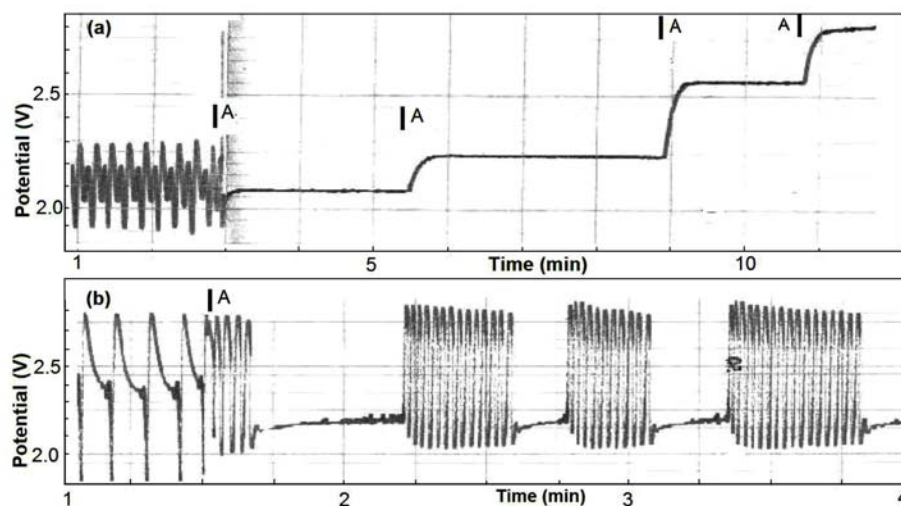


Fig. 2. Influence of Zn^{2+} ions on shape, amplitude and duration of the cell potential oscillations: (a) initial nitric acid:potassium dichromate molar ratio is 2.5 (50 ml nitric acid 1 M + 50 ml potassium dichromate 0.4 M) and (b) initial nitric acid:potassium dichromate molar ratio is 4.17 (50 ml nitric acid 1 M + 30 ml potassium dichromate 0.4 M). At the points marked with A, 1 ml of a 0.1 M Zn^{2+} solution were added.

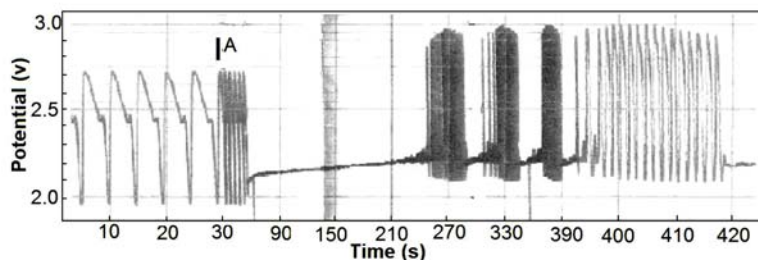


Fig. 3. Influence of Fe^{3+} ions on shape, amplitude and duration of the cell potential oscillations. Initial solution contained a nitric acid:potassium dichromate molar ratio of 2.5 (50 ml nitric acid 1 M + 50 ml potassium dichromate 0.4 M). At the point marked with A, 1 ml of a 0.1 M Fe^{3+} solution was added.

and Fe^{3+} addition on the dynamic behavior of the zinc/nitric acid + potassium dichromate/Pt system. As one can observe, in all the cases the complexity of the oscillations decreases. Chaotic behavior is reduced to simple oscillations whose duration and shape are different, depending upon the amount of cation added.

Each figure represents a part of the obtained recording and solution was added. The amplitude and the frequency of the shows only the changes that occur when metallic cation

oscillations depend upon initial electrolyte composition. Because this kind of systems is very sensitive to the initial conditions, the shape of oscillations at the same initial molar ratio nitric acid/potassium dichromate may be a little different. To reproduce identical initial conditions was a major impediment that we encountered in our works which is the common problem for studies of this nature. The time scale is arbitrary, but as time interval ratio is real.

Cu^{2+} ion leads to very regulated period-one oscillations

with about 600 mV amplitude and 0.1 s^{-1} frequency (Fig. 1a and 1b). As the quantity of Cu^{2+} added increases, oscillations become of relaxation type (Fig. 1c), less uniform and decreased duration. In this case, the electrode surface is covered by a very thin layer of copper, which determines the passivization of the electrode and oscillations cease.

In the case of Zn^{2+} ions addition (Fig. 2), one can observe two situations. First, at a nitric acid:potassium dichromate molar ratio of 2.5, the addition of zinc ions determines the oscillations disappearance, but each extra quantity leads to a potential jump. Probably, due to an increasing of zinc ions concentration near the electrode surface, the deposition rate of zinc compounds is bigger than the rate of their dissolution and oscillatory behavior of the electrode stops. If the molar ratio acid:dichromate increases (the second situation), at the same quantity of the added zinc ions, chaotic behavior turns into simple period-one oscillations zones connected by no oscillations periods. The amplitude of oscillations decreases (from about 950 mV to about 800 mV) and the frequency is around 0.15 s^{-1} . When zinc ions concentration near the electrode surface rises to above a critical threshold, the electrode passivates until the H^+ ions migrating from the bulk attain their critical concentration threshold for starting the oscillations again.

For iron(III) ions addition, the behavior of the system is the same as the second case of zinc. Groups of oscillations appear, but in this case, Fe^{3+} to Fe^{2+} reduction is involved followed by the reduction of Fe^{2+} , and Fe deposition to the electrode surface occurs. These electrochemical processes occur near the electrode surface, where the concentration of the oxidizing species is lower than in the bulk. The necessary potential is given by zinc oxidation. A slight increasing of the oscillations amplitude occurs (800 to 900 mV) and their frequency is about 0.7 s^{-1} .

CONCLUSIONS

Zinc anode behavior depends upon certain conditions like electrolyte composition [18], nitrate ions addition [17], metallic ions presence and others. If we accept that the potential (or current) oscillations are the results of the coupling of many active zones on the electrode surface, zones which behave like independent oscillators, then, the more the

oscillators, the more the complex oscillations. The oscillatory behavior of zinc electrode is induced by $\text{Zn}(\text{OH})_2$ precipitation-dissolution, depending upon H^+ ions concentration near the electrode surface. The addition of metal ions will result in an increase in positive charge density, other than H^+ ions, near the electrode. Thus, many active zones on the electrode surface become inactive and the complexity of the oscillations decreases.

Further study is needed to find exactly where the limit of cations concentration for leading to a precise behavior of zinc electrode is. This method may be applied for the dynamic behavior of zinc electrodes and chaos attenuation.

REFERENCES

- [1] J.L. Hudson, M.R. Basset, *Rev. Chem. Eng.* 7 (1991) 111.
- [2] O. Teschke, D.M. Soares, F. Galembeck, *J. Electrochem. Soc.* 132 (1985) 741.
- [3] C. Naitao, Z. Shiyong, W. Chao, C. Shenhao, *J. Serb. Chem. Soc.* 66 (2001) 563.
- [4] L. Organ, I.Z. Kiss, J.L. Hudson, *J. Phys. Chem. B* 107 (2003) 6648.
- [5] T.T. Lunt, J.R. Scully, V. Brusamarello, A.S. Mikhailov, J.L. Hudson, *J. Electrochem. Soc.* 149 (2002) B163.
- [6] P. Parmananda, B.J. Green, J.L. Hudson, *Phys. Rev. E* 65 (2002) 035202.
- [7] W. Wang, I.Z. Kiss, J.L. Hudson, *Ind. Eng. Chem. Res.* 41 (2002) 330.
- [8] I.Z. Kiss, J.L. Hudson, *Phys. Chem. Chem. Phys.* 4 (2002) 2638.
- [9] B.J. Green, J.L. Hudson, *Phys. Rev. E* 63 (2001) 026214.
- [10] W. Wang, B.J. Green, J.L. Hudson, *J. Phys. Chem. B* 105 (2001) 7366.
- [11] B.J. Green, W. Wang, J.L. Hudson, *Forma* 15 (2000) 257.
- [12] I.Z. Kiss, V. Gaspar, L. Nykos, *J. Phys. Chem. A* 102 (1998) 909.
- [13] K. Agladze, S. Thouvenel-Romans, O. Steinbock, *Phys. Chem. Chem. Phys.* 3 (2001) 1326.
- [14] J. St-Pierre, D.L. Piron, *J. Electrochem. Soc.* 137

Influence of Metal Ions on Oscillatory Behavior

- (1990) 2491.
- [15] J.L. Hudson, T.T. Tsotsis, Chem. Engng. Sci. 49 (1994) 1493.
- [16] N. Potkonjak, L. Kolar-Anić, T. Potkonjak, S.N. Blagojević, S. Anić, Mater. Sci. Forum 518 (2006) 301.
- [17] F. Crisan, E. Salló, Rev. Roum. Chim. 52 (2007) 661.
- [18] F. Crisan, E. Salló, J. Serb. Chem. Soc. 73 (2008) 221.