CCA-695 541.138:620.193
Conference Paper

Redox Reactions on Anodised or Passivated Metals*

B. Lovreček, B. Babić, I. Eškinja, O. Korelić, and N. Petric

Institute of Electrochemistry and Electrochemical Technology, Faculty of Technology, University of Zagreb, 41000 Zagreb, Croatia, Yugoslavia

Received February 11, 1972

The simple redox reactions on anodised or passivated metal (Al, Fe, Zn) were investigated by the current-potential method. The redox systems were chosen so that the electrochemical reaction was practically under the control of the diffusion in the electrolyte in case of unhindered charge transfer in the solid phase and on the contact electrode/electrolyte. Measurements were performed in a wider potential range, but on the previously anodised or passivated metal, in which case the potential range investigated was within the limits corresponding to low equivalent corrosion currents for the pure supporting electrolyte. In all the investigated cases the phenomena were observed, showing that the electron structure of the solid phase and possible potential barriers of the metal/phase layer/solution system had a predominant influence.

INTRODUCTION

Redox reactions on passivated metals have been mainly treated from two aspects in investigations up till now:

1) in order to obtain an insight into electrocatalytic properties of passivated electrodes, and

2) in concatenation with investigations of passivating inbihitors.

The characteristic of these investigations has mainly been the observation of the solid/solution interface, whereas the influence of phase oxide bulk on the overall process has been less frequently treated. It has been generally considered that the redox reaction on passivated metal, if a sufficient value of potential has been achieved, occurs often so easily that is is limited only by the rate of charge transport in the solution. Our investigations have been undertaken in order to recheck this assumption with model redox reactions, chosen so as to take place practically under the control of diffusion in the solution if not hindered by the phase layer. For comparison, the redox processes have been parallelly investigated on the platinum electrode under as identical conditions as possible.

EXPERIMENTAL

Investigations were performed on the passivated electrodes of zinc and iron, as well as on the anodised aluminium. The oxide layer on the Al-electrode (99.99%) was formed by anodic oxidation of super-purity aluminium in the 0.5 *M* solution of H_3BO_3 at 100 V.

---

* Based on a lecture presented at the *22nd Meeting of the International Society of Electrochemistry,* Dubrovnik, Yugoslavia, September 1971.

The passivation of the Zn-electrode (min. purity 99.9%) was performed in the 0.01 *N* solution of KOH at the potential of 1650 mV. The passivation of the Fe-electrode (Armco iron) was performed in the 0.075 *N* solution of H_3BO_3 and $Na_2B_4O_7$ at the potential of 800 mV. The measuring of the current-potential curves was made by the classic steady state method. All the quoted potentials are given with respect to the standard hydrogen electrode.

The measurement of the current-potential curves for the redox system potassium ferrocyanide-potassium ferricyanide was performed in nitrogen atmosphere, respectively argon one whereas the oxygen reduction was made in the atmosphere of oxygen, respectively of air. All the experiments were performed at temperature of 25° C.

RESULTS

1. Redox System Potassium Ferrocyanide-Potassium Ferricyanide

The current-potential curves, obtained by performing the cathodic and anodic polarization on the platinum electrode show the expected well-expressed plateaus of the limiting current both on the cathodic and on the anodic side.

Fig. 1. represents polarization curves on the anodized Al-electrode and Pt-electrode in the 0.5 *M* solution of H_3BO_3 (*p*H — 8.9, adjusted by ammonia) with and without the addition of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ in several different concentration ratios.

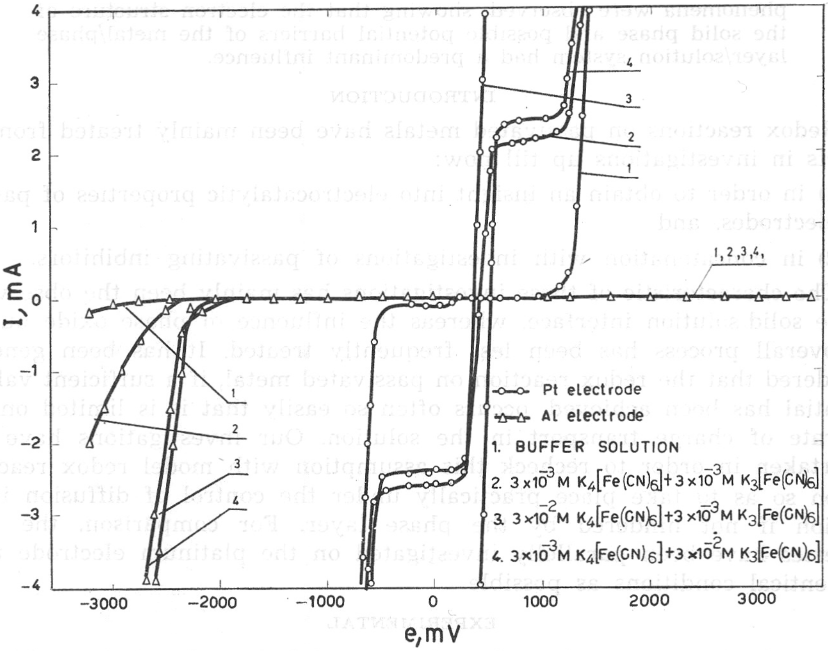

Fig. 1. Polarization curves on the anodised Al-electrode and Pt-electrode in the 0.5 *M* solution of H_3BO_3 with and without the addition of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$.

From Fig. 1. it can be seen that the oxide layer on aluminium represents a barrier to the current in the anodic direction (measured up to the potential of 3 V). In the cathodic direction in the investigated potential range (up to

— 3 V) the plateau of the limiting current in the presence of the ferricyanide ion is absent, the curves are considerably shifted to a more negative potential region with respect to the Pt-electrode, but the rise of the current occurs earlier than on the anodised electrode without the presence of the ferricyanide ion. Furthermore, it is evident that cathodic currents higher than the limiting currents for the reduction of the ferricyanide ion can be achieved, and that they show a dependence on the concentration ratio of the ferrocyanide and ferricyanide ion.

In the course of measurements characteristic changes of the current with time were also observed at a given potential and in the presence of the redox system.

Fig. 2. gives the polarization curves on the passivated Zn-electrode and Pt-electrode in the 0.01 *N* solution of KOH with the addition of $K_4 Fe(CN)_6$ and $K_3Fe(CN)_6$ in several different concentration ratios. As the effects obtained on the passivated zinc are identical to the ones on the passivated iron, they will be commented together.

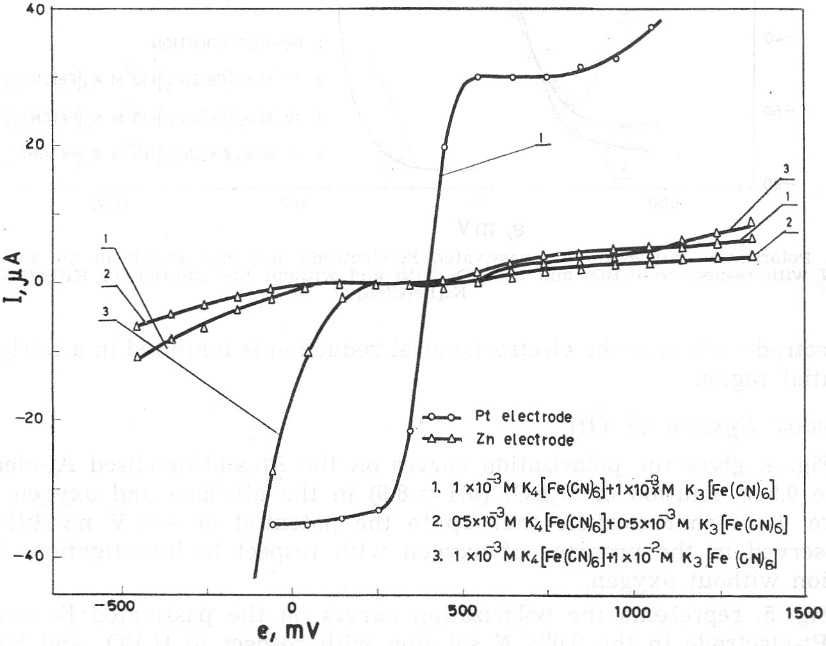

Fig. 2. Polarization curves on the passivated Zn-electrode and Pt-electrode in the 0.01 *N* solution of KOH with the addition of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$.

Fig. 3. represents the polarization curves on the passivated Fe-electrode and Pt-electrode in the solution of 0.075 *N* with respect to H_3BO_3 and $Na_2B_4O_7$ with and without the addition of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ in several different concentration ratios.

In systems with the passivated Zn and Fe electrodes typical limiting currents are observed in the anodic part, but considerably lower than on the

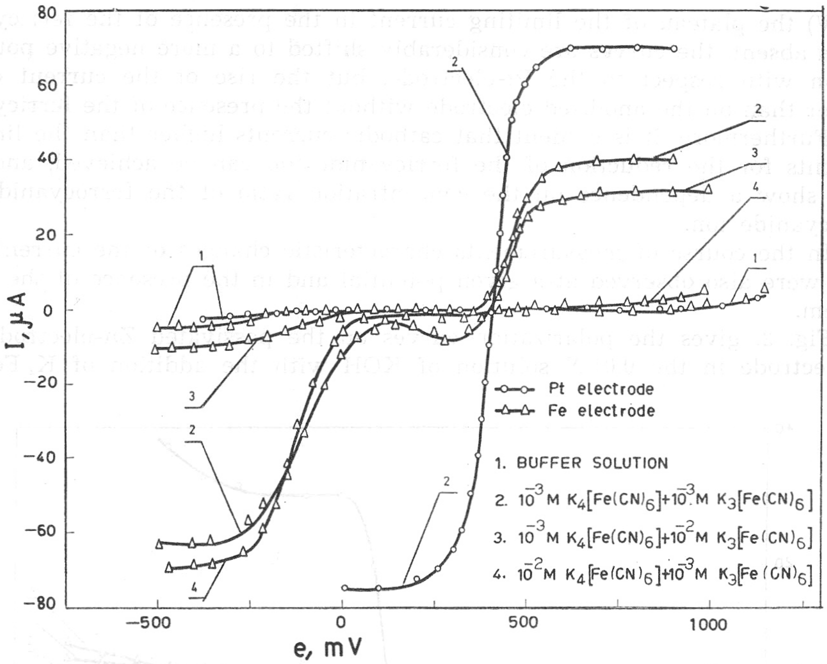

Fig. 3. Polarization curves on the passivated Fe-electrode and Pt-electrode in the solution of 0.075 *N* with respect to H_3BO_3 and $Na_2B_4O_7$ with and without the addition of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$.

Pt-electrode, whereas the electrochemical reduction is inhibited in a fairly wide potential region.

2. *Redox System* O_2/OH^-

Fig. 4. gives the polarization curves on the Pt and anodised Al-electrode in the 0.5 *M* solution of H_3BO_3 ($pH = 8.9$) in the nitrogen and oxygen atmosphere. It is characteristic that up to the potential of — 3 V no difference is observed in the presence of oxygen with respect to investigations in the solution without oxygen.

Fig. 5. represents the polarization curves on the passivated Fe-electrode and Pt-electrode in the 0.075 *N* solution with respect to H_3BO_3 and $Na_2B_4O_7$ in the nitrogen and air atmosphere. The polarization curve on the passivated Fe-electrode is shifted to a more negative region of the potential with respect to the Pt-electrode, identical to the ones in the presence of the ferricyanide ion.

DISCUSSION

The above observations about the behaviour of all systems investigated can be grouped according to the following characteristics:

1) The introduction of the redox system into the starting solution on the passivated, and anodized metals investigated resp., causes always, expect for the Al/oxide layer/solution system, saturated with oxygen, differences with respect to the solution without the redox couple.

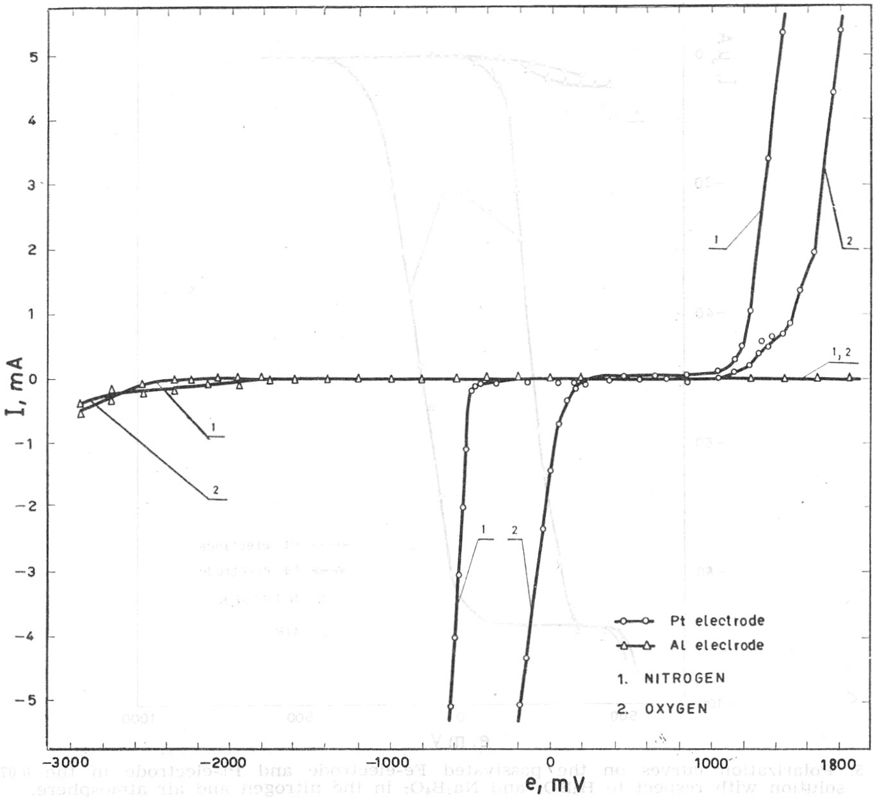

Fig. 4. Polarization curves on the anodised Al-electrode and Pt-electrode in the 0.5 *M* solution of H_3BO_3 the nitrogen and oxygen atmosphere.

2) For the same electrochemical reactions on the passivated and anodized metals, resp., differences are observed with respect to the Pt-electrode, consisting either in the shift of the potential, or in the occurrence of the limiting current independent of the diffusion of the reacting species in the solution..

Cathodic processes. — Considering the cathodic polarization of systems investigated a common characteristic is observed: considerable shifts of the potential to the negative side with respect to the ones on the Pt-electrode, respectively from the steady state potentials, where otherwise anodic reactions on passivated metals (Zn, Fe) began. This shows:

1) that on the typical valve metal (Al) there is a considerable barrier action also in the so-called forward direction, and

2) that such properties of conductivity should not, as a rule, be exclusively connected with the so-called valve metals, as the same property is shown also by the passive metals.

However, there are also certain specific features in their behaviour. Although the treatment of the insulating electrode could be applied for cathodic reactions on the passivated zinc and iron, as it will be done for anodic reactions on them, there are some other factors of influence here. Due to this

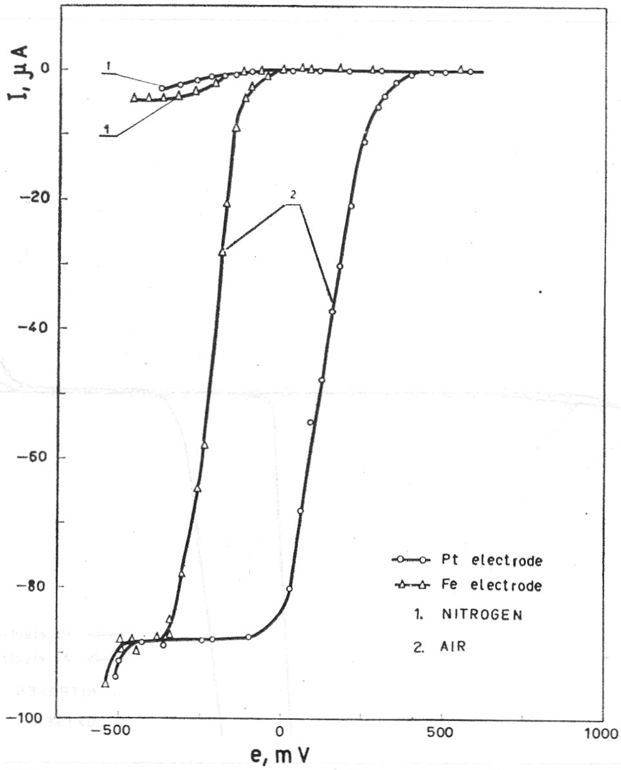

Fig. 5. Polarization curves on the passivated Fe-electrode and Pt-electrode in the 0.075 *N* solution with respect to H_3BO_3 and $Na_2B_4O_7$ in the nitrogen and air atmosphere.

fact and the fact that in some cases the region of the instability of passive oxide films[1] is entered by the cathodic polarization, a more detailed discussion of these results will not be made now. Two facts seem to be very important in the cathodic process on the anodised aluminium:

1) that the increase of the current in the presence of the redox system ferrocyanide/ferricyanide occurs before the increase of the current in the starting electrolyte, but still at the potential for almost 3 V more negative than the reversible potential, and

2) currents occurring here can be higher than the limiting currents determined by the diffusion of the ferricyanide ion in the solution.

The shift of the reduction potential indicates a certain »barrier action« in the otherwise forward direction, due probably to the structure of the oxide layer and its ability to form potential barriers. Thus, *e. g.*, there is a possibility of a rectifying contact between the metal base and the n-type layer. On an Al/oxide layer/Hg system, though a different one, the effective rectification in the direction reverse to the usual one was observed[2]. A further possibility would be in the treatment of the layer as insulating electrode with the injection of the charge carriers from the solution. The results of these investigation show that the oxide layer/electrolyte contact plays a certain role, but the situation is, evidently complex. Our results have undoubtedly shown that in the presence of the redox system a considerable increase of the cathodic current occurs in comparison to the system which does not contain a redox system. This occurs also even in amounts higher than the limit diffusion currents in the solution for the reduction of ferric ions which, accordingly in a broader sense, cause a catalytic effect with the participation of the solid phase. The penetration of protons[3-5] can also represent an important factor in the behaviour of the electrode.

This points to a complexity of the mechanism of the effect to the present redox system. Moreover, it has been analytically* established that the net changes due to the cathodic reduction of ferricyanide are practically, not present.

Our results indicate the fact that the presence of the redox system facilitates the penetration of protons into the solid phase, which, in turn, then increases the cathodic current, as earlier suggested by Hale[5]. It is of interest that in the case of the presence of oxygen in the solution, although there is a certain inhibition, there is practically no change of the cathodic current in the region of investigated cathodic potentials.

Anodic processes. — Considering the anodic polarization of systems investigated it has already been stated that the oxide layer on aluminium represents a barrier to the current in the anodic direction (measured up to the potential of 3 V), whereas the characteristics of polarization curves on the passivated iron and zinc are identical, *i. e.* at anodic polarization limiting currents appear, being evidently dependent on the concentration of the ferrocyanide ion. However, the observed limiting currents in the presence of the redox system are lower than the limiting currents obtained under the same hydrodynamic conditions on the Pt-electrode. Consequently, the limiting currents in these two systems are not determined by the diffusion in the solution. Similar observations are found — though more rarely — in literature[6]. Accordingly, the phenomenon of limiting currents is due to the occurrences in the solid phase of the system or on its very surface. Here there are several possibilities, such as:

1) diffusion of charge carriers in the solid phase;

2) limited injection of charge carriers from the solution into the solid phase;

3) creation of surface states by adsorption, *etc.*

The first possibility, though worthy of consideration due the probable *n*-type character of passive films, is less probable on the passivated zinc and iron, due to the very limited thickness of passive layers. Besides, the influence of the concentration of the ferrocyanide ion on the limiting current could not be expected. Furthermore, we are inclined to give a preference to the second possibility, *i. e.* to the injection of charge carriers from the electrolyte, instead of to the third one, which would require a formation of surface states by the adsorption of the reacting species from the solution.

---

* These investigations were performed after the *22nd Meeting of ISE* and they will be reported on another occasion.

Accepting such an assumption, Hale's[5] suggestion can be applied, treating anodic films as insulators with the injecting contact towards the solution. In such a case the already elaborated theory of the insulating electrode can be applied. The possibility of the appearance of limiting currents, dependent on the concentration of the reacting species in the solution, has been of greatest interest for us in such a conception. Namely, the limiting current is equal to the exchange current for the redox reaction on the insulating electrode[7]:

$$i_1 = i_o^s$$

and, consequently, our results offer a possibility of determining the exchange current for the corresponding redox system on the oxide layer. Using the well-known expression of Dogonadze and Chizmadzhev[8], the difference between the Fermi level of the insulator and the carrier band on the surface at equilibrium can be also determined:

$$i_o^s = i_o^M \exp\left(-\frac{\overline{\Delta}}{2\,kT}\right)$$

The application of these expressions to our investigated systems at the same concentrations of the ferrocyanide and ferricyanide ions 10^{-3} *M*, has given the following results:

for the passivated iron $\overline{\Delta} = 0.22$ eV

for the passivated zinc $\overline{\Delta} = 0.27$ eV

Both values seem to be quite probable, and such an approach to the treatment of the passivity in investigated cases seems to be justified.

Although the dependence of the observed limiting currents in our systems corresponds generally to the theory, some problems might arise in the quantitative treatment, but we have not enough experimental material for the present to say something definite on it.

CONCLUSION

This survey of some of our investigations from the electrochemistry of valve and passivated metals seems to us to indicate that such systems should not be treated separately as quite different phenomena. Investigations in this respect have been proceeding.

REFERENCES

1. N. Sato and K. Kudo, *Electrochim. Acta* **16** (1971) 447.
2. O. Korelić and B. Lovreček, *Symposium sur les Bauxites,* Zagreb, (1963) 127.
3. P. F. Schmidt, *J. Appl. Phys.* **28** (1957) 278.
4. D. A. Vermilyea, *J. Phys. Chem. Solids* **26** (1965) 113.
5. J. M. Hale, *J. Electrochem. Soc.* **115** (1968) 208.
6. A. C. Makrides, *J. Electrochem. Soc.* **111** (1964) 392.
7. W. Mehl and F. Lohmann, *Electrochim. Acta* **13** (1968) 1459.
8. R. R. Dogonadze and Yu. Chizmadzhev, *Dokl. Akad. Nauk SSSR* **150** (1963) 333.

IZVOD

Redoks reakcije na anodiziranim ili pasiviranim metalima

B. Lovreček, R. Babić, I. Eškinja, O. Korelić i N. Petric

Jednostavne redoks reakcije na anodiziranom ili pasiviranom metalu (Al, Fe, Zn) su ispitivane struja-potencijal metodom. Redoks sistemi su odabrani tako, da u slučaju nesmetanog prenosa naboja u čvrstoj fazi i na granici elektroda/elektrolit elektrokemijska reakcija je praktički pod kontrolom difuzije u elektrolitu. Mjerenja su izvršena u širem području potencijala, ali na prethodno anodiziranom metalu ili prethodno pasiviranom metalu u kojem slučaju se istraživano područje potencijala nalazi unutar granica koje odgovaraju niskim ekvivalentnim korozionim strujama za čisti osnovni elektrolit. U svim istraživanim slučajevima opaženi su fenomeni koji pokazuju da elektronska struktura čvrste faze i moguće potencijalne barijere sistema metal/fazni sloj/otopina imaju odlučujući utjecaj.

ZAVOD ZA ELEKTROKEMIJU
I
ELEKTROKEMIJSKU TEHNOLOGIJU
TEHNOLOŠKI FAKULTET SVEUČILIŠTA
41000 ZAGREB

Primljeno 11. veljače 1972.