Journal of Applied Electrochemistry **32**: 1379–1382, 2002.

Rectification behaviour of some metal ion–metal interfaces and concentration cells

K.K. AGARWAL[1],* and H.P. AGARWAL[2]
[1]*Department of Computer Science, Louisiana State University in Shreveport, Shreveport, LA 71115, USA;*
[2]*E7/H508, Arera Colony, Bhopal, India 462016*
*(*author for correspondence, fax: +1 318 795 4221, e-mail: kagarwal@pilot.lsus.edu)*

Received 3 October 2001; accepted in revised form 6 September 2002

Key words: concentration cells, diode behaviour, metal ion–metal interface

Abstract

The rectification behaviour of three metal ion–metal interfaces and 38 concentration cells was studied. The rectification in $Al|Al^{3+}|Al$ was 35% (−0.4 to +0.80 V d.c.) between 2.0–5.0 V a.c. and for $Zn|Zn^{2+} \vdots Al^{3+}|Al$ cell was 20% (+0.20 to −0.30 V d.c.). Its negative d.c. potential showed some similarity to a tunnel diode. 20% rectification was obtained when each of Al, Zn, Mg half-cell was coupled with I^-, $I_2|$ Pt half-cell and Al half-cell was coupled with Fe^{3+}, $Fe^{2+}|$Pt half-cell. When the Zn half-cell was associated with Cr^{3+}, $Cr_2O_7^{2-}|$Pt half-cell the rectification was 15%, whereas the rectification in all other concentration cells varied from 1 to 12%. The possibility of obtaining much higher percentage of rectification can be explored in a large number of other metal ion–metal interfaces and concentration cells which can be assembled in a similar manner using the table of standard reduction potentials. The characteristics of a concentration cell can be varied by change in concentration of metal ion, redox ratio, variation of pH, temperature, effect of different additives to the cell solution, irradiation of electrode surface etc. Consequently, it will affect the percentage of rectification which may be of some use in commercial applications.

1. Introduction

When two platinum electrodes dipped in aqueous solution containing a redox couple are connected to an a.c. source, a rectified potential is developed at each of these electrodes. This phenomenon has been termed faradaic rectification and was discovered in 1950 by Doss and Agarwal [1]. The rectification of a.c. by an electrode reaction in redox and concentration cells arises due to the asymmetry of the current versus potential curve. The asymmetry of these curves results from the intrinsic asymmetry of the charge transfer reaction or from the extraneous asymmetry produced by inequalities in mass transfer rates of oxidants and reductants. The beta values for anodic half-wave and cathodic half-wave polarization are not identical or ever equal to 0.5. The schematic representation when either the alternating current or alternating voltage is controlled across the faradaic impedance giving rise to rectification voltage and other related details are discussed in the earlier review on faradaic rectification in 1974 [13]. The faradaic rectification results because of faradaic distortion and both of these phenomena are interdependent.

Soon after the discovery of this effect, other related non-linear phenomena such as radio-frequency polarography [2, 3], second harmonics polarography [4, 5], intermodulation polarography [3, 6], and high level faradaic rectification [3, 7] were developed for the study of fast electrode reactions. The faradaic rectification studies have also been carried out with semiconductor–electrolyte interfaces [8]. Delahay et al. [9, 10] gave an elegant treatment and developed the technique for study of fast electrode reactions at radio frequencies. The kinetic parameters of fast electrode reactions at redox couple–metal, metal ion–metal, mercuric ion–mercury [11] and metal ion–amalgam [12] interfaces have been given in an earlier review on the subject in 1974 [13].

The faradaic rectification method was applied for the first time for determining the kinetic parameters for each step of electron transfer [14] in a multiple electron charge-transfer reaction ($M^{3+} + e^- \rightarrow M^{2+} + e^- \rightarrow M^+ + e^- \rightarrow M$) and for developing faradaic rectification polarography which enabled study of kinetic parameters of several organic reactions [15]. A second review on the work done on the subject after 1972 has appeared in 1989 [16]. In the present work, rectification by a few metal ion–metal interfaces and concentration cells was studied to explore their conventional diode behaviour.

To meet a wide variety of requirements, different types of rectifiers are used for converting alternating into direct current. These are mostly dry metal or solid-state semiconductors. Diodes are also used for signal detection, clipping of waveforms, voltage regulation, and capacitor filter circuits.

The work discussed in this paper could lead to liquid-junction diodes or possibly even transistors. Transistors are well known to have many applications. It would be interesting to study the characteristics of such devices and to find new applications for them.

2. Experimental details

For studying rectification characteristics, the conventional diode in series with the a.c. source and the filter was replaced by the metal ion–metal interface or concentration cell connecting the positive end of the cell to the positive terminal of the multimeter. The d.c. potential across the filter was measured at varying a.c. voltages. As the concentration cell comprises a salt solution in aqueous or in acidic media to prevent hydrolysis, the studies were carried out at 30 °C up to 5.0 V a.c. (to avoid evolution of hydrogen and oxygen gases). The mains a.c. source (110 V, 60 Hz) was connected to a step-down transformer of 10 V which in turn was connected to a potentiostat to tap a.c. from 0 to 5 V. The filter was a simple device connecting a resistor to a ceramic capacitor of 10 μF in parallel across which the d.c. potential was measured by a multimeter (Keithley 168 autoranging DMM) having an internal resistance of 10 MΩ. The ground of the potentiostat, filter and multimeter was common. It was observed that if the value of the resistor used in the filter circuit matches, in general, with the internal resistance of the cell (which was determined experimentally for each cell) only pure d.c. was obtained. The filter circuit waveform was a full sine wave as was the a.c. input voltage.

The concentration cells were composed of metal ion–metal half-cells given above the $2H^+ + 2e^- \rightarrow H_2$ reaction and some redox half-cells falling below the reversible hydrogen potential. When two electrodes of the same metal are dipped in a solution containing the same metal ion (e.g., $Zn|Zn^{2+}|Zn$) this constitutes a cell of metal ion–metal interfaces. The other two metals selected for such studies were Mg and Al. Two different metal ion–metal half-cells combined to form a concentration cell (e.g., $Mg|Mg^{2+} \vdots Zn^{2+}|Zn$). When the $Al^{3+}|Al$ half-cell was coupled with the $Mg^{2+}|Mg$ and $Zn^{2+}|Zn$ half-cells, respectively, two more cells were obtained. An Agar gel aqueous solution saturated with NaCl was used as the liquid–liquid junction bridge. In all the experiments, analytical grade metal and salts were used. The results obtained are shown in Figure 1. The rectification percentage is shown in brackets, corresponding to each plot in all the figures.

The other concentration cells studied were set up by associating half-cells of metal ion–metal with a redox couple half-cell (e.g., Fe^{3+}, $Fe^{2+}|Pt$). The metal ion–metal half-cells chosen were $Mg^{2+}|Mg$, $Al^{3+}|Al$, $Zn^{2+}|Zn$, $Fe^{2+}|Fe$, $Cd^{2+}|Cd$, $Sn^{2+}|Sn$, $Ni^{2+}|Ni$, whereas the other redox half-cell reactions selected were Sn^{4+}, $Sn^{2+}|Pt$, I^-, $I_2|Pt$, Mn^{2+}, $MnO_2|Pt$ and Cr^{3+}, $Cr_2O_7^{2-}|Pt$. Seven different concentration cells were formed when each metal ion–metal half-cell was coupled with one particular redox half-cell (e.g., Fe^{3+}, $Fe^{2+}|Pt$). In all, five redox couples were selected which leads to a series of 35 concentration cells.

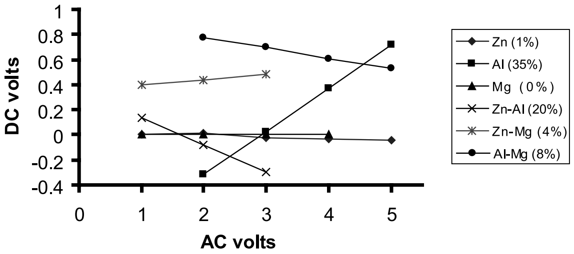

Fig. 1. Rectified potential against a.c. voltage; (a) study of metal | metal ion | metal cell (both electrodes of the same metal); metal – Mg, Al, Zn, (b) study of concentration cells e.g., $Mg|Mg^{2+} \vdots Zn^{2+}|Zn$; $Al^{3+}|Al$, replaces Mg or Zn reversible electrode in the other two cells (represented as Mg–Zn, Al–Zn, Mg–Al).

The oxidant and reductant salts were dissolved in 0.5 M sulfuric acid except KI and I_2 which were dissolved in water. Agar gel aqueous solution, saturated with NaCl, was used as a bridge to avoid liquid–liquid junction potentials. The results obtained are given in Figures 2 to 6, each corresponding to a particular redox couple.

The extent of rectification by any reversible or concentration cell depends on the nature of the half-cells constituting the cell. The rectification is linear at varying ranges 0.5–3.0 V, 0.5–4.0 V, 0.5–5.0 V, 1.0–3.0 V, 1.0–4.0 V and 2.0–5.0 V a.c. depending upon the nature of the cell (Figures 1–6).

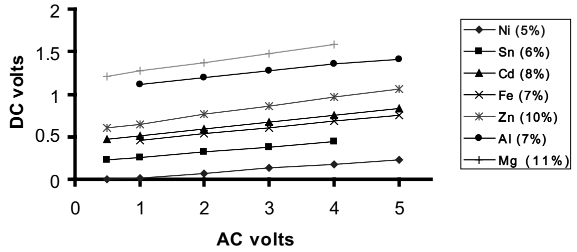

Fig. 2. Rectified potential against a.c. voltage. Study of the metal | metal ion $\vdots$ Sn^{4+}, $Sn^{2+}|Pt$ cell; metal – Mg, Al, Zn, Fe, Cd, Sn, Ni.

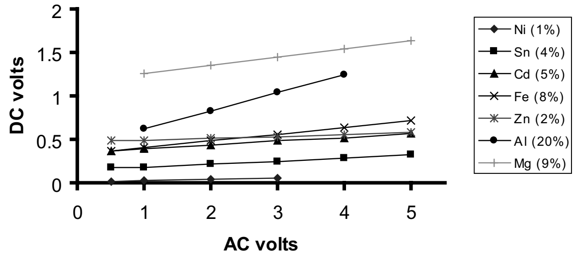

Fig. 3. Rectified potential against a.c. voltage. Study of the metal | metal ion $\vdots$ Fe^{3+}, $Fe^{2+}|Pt$ cell; metal – Mg, Al, Zn, Fe, Cd, Sn, Ni.

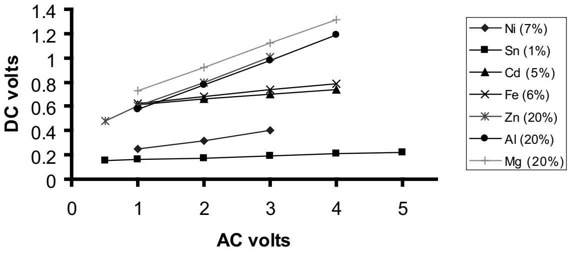

Fig. 4. Rectified potential against a.c. voltage. Study of the metal | metal ion ⋮ I^-, I_2|Pt cell; metal – Mg, Al, Zn, Fe, Cd, Sn, Ni.

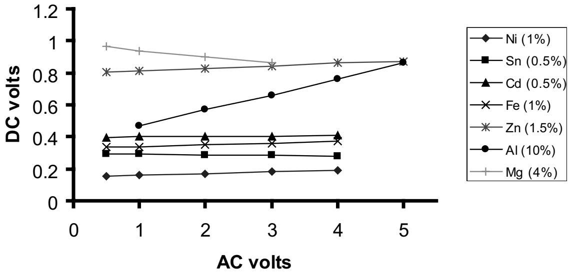

Fig. 5. Rectified potential against a.c. voltage. Study of the metal | metal ion ⋮ Mn^{2+}, MnO_2|Pt cell; metal – Mg, Al, Zn, Fe, Cd, Sn, Ni.

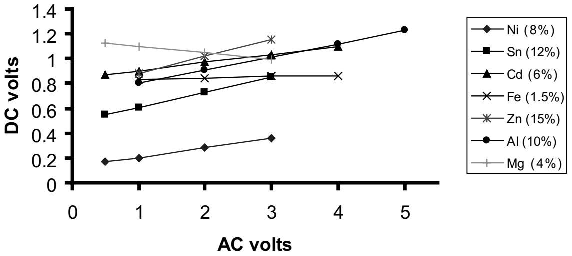

Fig. 6. Rectified potential against a.c. voltage. Study of the metal | metal ion ⋮ Cr^{3+}, $Cr_2O_7^{2-}$|Pt cell; metal – Mg, Al, Zn, Fe, Cd, Sn, Ni.

3. Results and discussion

3.1. *Metal ion–metal interfaces*

The Al|Al^{3+}|Al cell rectification was 35% between 2.0 to 5.0 V a.c. covering a wide range of d.c. from −0.40 to +0.80 V (Figure 1). This may be due to the triple valency of the metal and because the potential difference between the two electrodes of the cell being almost zero (accounting for variation of d.c. from negative to positive values). In the case of the Zn|Zn^{2+}|Zn cell, the rectified potential was also negative and was only 1.0%. The cell formed by Mg^{2+}|Mg showed practically no rectification which may perhaps be due to the fact that only an aqueous solution of a magnesium salt was used to avoid hydrogen evolution (the internal cell resistance being high). When Zn^{2+}|Zn formed a concentration cell in association with the Al^{3+}|Al half-cell, the rectification was 20% (d.c. varies from +2.0 to −0.30 V). This behaviour was somewhat similar to that of a tunnel diode and was due to the influence of the Al half-cell component of the composite cell.

Similarly, when the Zn half-cell was coupled with the Mg^{2+}|Mg half-cell, rectification was 4% (d.c. positive). The concentration cell formed with Mg^{2+}|Mg and Al^{3+}|Al half-cells gave 8% rectification (d.c. positive but with a negative slope). In the table of standard reduction potentials, the Mg half-cell reduction potential is −1.85 V, which is much higher compared with that of the Al or Zn half-cell reduction potentials; this accounts for the rectification potential being positive.

3.2. *Metal–metal ion* ⋮ *Sn^{4+}, Sn^{2+}|Pt*

Seven cells were set up by coupling each of the Mg^{2+}|Mg, Al^{3+}|Al, Zn^{2+}|Zn, Fe^{2+}|Fe, Cd^{2+}|Cd, Sn^{2+}|Sn, Ni^{2+}|Ni half-cells individually with the Sn^{4+}, Sn^{2+}|Pt half-cell. The rectification behaviour for each of them was studied at varying a.c. between 0.5 to 5.0 V (Figure 2).

The rectification for cells formed with Ni^{2+}|Ni, Sn^{2+}|Sn, Cd^{2+}|Cd, Zn^{2+}|Zn varied linearly in the increasing order, 5, 6, 8 and 10%, respectively. In the case of cells set up with the Fe^{2+}|Fe, Al^{3+}|Al, Mg^{2+}|Mg, couples the rectification was linearly proportional to the a.c. amplitude; with the first two half-cells the rectification was 7% whereas for the latter it was 11%.

3.3. *Metal–metal ion* ⋮ *Fe^{3+}, Fe^{2+}|Pt*

Using the seven metal ion|metal half-cells constituted by Mg, Al, Zn, Fe, Cd, Sn, Ni metals and combining each of them separately with the Fe^{3+}, Fe^{2+}|Pt redox half-cell, seven concentration cells were assembled. Their rectification characteristics were studied (Figure 3). The rectification percentage with the Al half-cell was 20%, for the Mg half-cell, it was 9% and for others it varied from 8% to 1%. It is rather unusual that Zn half-cell with this redox half-cell shows only 2% rectification.

3.4. *Metal–metal ion* ⋮ *I^-, I_2|Pt*

The concentration cells formed with this redox half-cell in association with the Zn^{2+}|Zn, Al^{3+}|Al and Mg^{2+}|Mg half-cells, the rectification was 20% (Figure 4) and, by varying the redox ratio, much higher degrees of rectification can be expected. The concentrations of KI and I_2 chosen in the present study were 0.1 M and 0.02 M, respectively, in aqueous solution. The rectification percentage varied from 7% for Ni^{2+}|Ni, 6% for Fe^{2+}|Fe, 5% for Cd^{2+}|Cd and 1% for Sn^{2+}|Sn.

3.5. *Metal–metal ion* ⋮ *Mn^{2+}, MnO_2|Pt*

This redox half-cell in association with the Al^{3+}|Al half-cell gave 10% rectification and the rectification with all other metal ion–metal half-cells was below 4% (Figure 5). This may perhaps be due to the fact that in 0.5 M sulfuric acid solution the reaction of MnO_2 is slow and the concentration of Mn^{4+} ions present in the redox half-cells is very small. However, by increasing the acid concentration there is a possibility of enhancing the rectification in such cells.

3.6. *Metal–metal ion* : Cr^{3+}, $Cr_2O_7^{2-}|Pt$

When this redox half-cell was combined with $Zn^{2+}|Zn$, $Sn^{2+}|Sn$, $Al^{3+}|Al$, $Ni^{2+}|Ni$ and $Cd^{2+}|Cd$ half-cells, respectively, their rectification varied in the order of 15, 12, 10, 8 and 6% (Figure 6). It was rather surprising that when the cells were formed with $Mg^{2+}|Mg$ and $Fe^{2+}|Fe$ half-cells the rectification was only 4 and 1%, respectively.

4. Conclusions

The extent of rectification by a concentration cell depended upon the nature of the two constituent half-cells. Among the five redox half-cells coupled with seven different metal ion–metal half-cells, pronounced rectification was obtained with the I^-, $I_2|Pt$ half-cell when it was coupled with half-cells of Al, Zn and Mg (20%); while Cr^{3+}, $Cr_2O_7^{2-}|Pt$ coupled with half-cells of Zn, Sn, Al, Ni gave rectification of 15–8%; whereas, Fe^{3+}, $Fe^{2+}|Pt$ on associating with half-cells of Al, Mg, Fe gave 20–8% rectification and on combining Sn^{4+}, $Sn^{2+}|Pt$ with half-cells of Mg, Zn, Cd, 11–8% rectification was observed. Only the $Al^{3+}|Al$ half-cell in combination with the Mn^{2+}, $MnO_2|Pt$ half-cell gave 10% rectification, whereas, with other metal half-cells, the rectification was below 4%. It was found that for getting higher percentage rectifications the half-cells of Al, Zn, Mg were preferable and with certain redox couple cells, Cd, Ni, Fe and Sn half-cells gave rectification from 8 to 12%.

The rectification of the interface cells formed by the three metals, respectively, varied in the order Al > Zn > Mg. It is worth noting that the $Al^{3+}|Al$ interface cell gave the highest rectification (35%) and it extended from −0.40 to +0.80 V d.c. between 2.0 and 5.0 V a.c. Similarly, in the concentration cell formed by $Zn^{2+}|Zn$ and $Al^{3+}|Al$ half-cells, the rectification was 20% and the d.c. varied from +2.0 to −0.30 V. The negative d.c. potential showed, to some extent, a behaviour analogous to that of a tunnel diode. In this respect the rectification by a metal ion–metal interface or a concentration cell has a distinct edge on a conventional diode and needs further exploration for its use in different applications.

The study of rectification by a concentration cell opens new research possibilities because the effect of variation of concentration of the metal ion, redox ratio, pH, temperature, effect of different additives, effect of light irradiation on elecrode surfaces, etc can be studied. Further, several other metal ion–metal interfaces and concentration cells can be assembled from the table of standard reduction potentials to explore the possibility of getting rectification matching that of a conventional diode.

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