

Electrochemical characterisation of porous iron electrodes

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Abstract. Porous iron electrodes containing metal additives have been used in nickel–iron cells. The impedances of these electrodes were measured over a wide range of frequency 10^4 Hz to 10^{-2} Hz in 6 M KOH + 0.63 M LiOH solutions. Using a cylindrical pore model, porosity and its related parameters were calculated. It is found that Hg and S provide favourable porosity and thus enhance the discharge capacity.

Keywords. Porous iron electrode; Faradic impedance; electrochemical characterisation.

1. Introduction

Major problems associated with alkaline porous iron electrodes are the high rates of self-discharge and the low efficiencies of utilisation of active iron. Additives are usually blended with electrode material to overcome these problems (Ojefors 1976; Vassie and Tseung 1976; Micka and Zabransky 1987; Jayalakshmi and Muralidharan 1991). The role of these additives in altering the physical structure and electrochemical behaviour is of fundamental interest. In this paper, impedance has been employed as a tool to analyse the changes occurring in the pore characteristics of sintered porous iron electrodes containing metal additives at -1000 mV and -700 mV vs Hg/HgO respectively.

2. Experimental

Two types of sintered electrodes were used which differ mainly in respect to active material impregnation. Porous iron electrodes were prepared from electrolytic iron powder (α -Fe of composition (W/W) 99.1% Fe, 0.01% Pb, 0.08% Zn, 0.001% As, 0.025% Mn and 0.005% Cu) and of -300 mesh particle size. The iron powder was spread uniformly in a graphite die over a 10-mesh nickel grid of 0.1 mm thickness. Sintering temperature and time were 1170 K and 60 min, respectively, in an atmosphere of hydrogen.

Loose sintered nickel electrodes were also prepared in a similar way from reduced INCO nickel 255 powder. The area and thickness of both iron and nickel electrodes were 1.6 cm² and 2 mm respectively.

Sintered iron electrodes of porosity [60–70%] were doped cathodically in 0.1 M

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solutions of lead acetate, mercury, silver and copper nitrates and sulphur in 6 M KOH. A cathodic current of 10 mA, from a constant current generator was applied for 10 min. The increase in weight gave the amount of metal ions incorporated.

In loose sintered nickel electrodes of porosity 70 to 80% the active material was electrochemically incorporated by using them as cathodes while nickel sheets of purity 99.5% and of size 5×1 cm were used as anodes. Impregnation was carried out using two anodes on either side of the cathode at the rate of 20 mA for 90 min in an electrolytic bath of composition 3 M $\text{Ni}(\text{NO}_3)_2$, 0.25 M $\text{CO}(\text{NO}_3)_2$, 0.1 M $\text{Cd}(\text{NO}_3)_2$ and 0.1 M MnSO_4 . The pH of the bath was adjusted by adding formic acid. After 90 min the electrode was immersed in hot alkali at 60°C for 30 minutes, rinsed with double distilled water and dried. This process was repeated till there was no appreciable change in weight.

3. Impedance measurements

Impedance measurements were carried out at fixed potentials using an AC impedance system [PAR Model 368, USA] comprising a Model 5206 two-phase lock in amplifier with Model 173 potentiostat/galvanostat. A three-electrode cell assembly consisting of iron as the working electrode, nickel as the counter electrode and Hg/HgO electrode as reference was employed. Impedance spectra were obtained for solid iron; porous iron and also for porous iron with additives at -700 mV and -1000 mV. These values of potential correspond to discharged and charged conditions of iron electrode respectively.

4. Results

4.1 Solid iron

Figure 1 presents the impedance plot of z' vs z'' (Nyquist plot) for a solid iron electrode at -1000 mV. Below 0.1 Hz, a Warburg impedance with a slope of 45° is obtained;

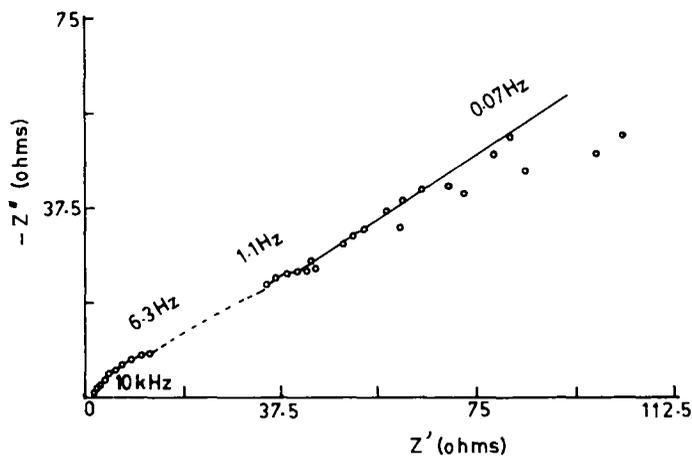


Figure 1. Impedance spectra for solid iron electrode at -1000 mV.

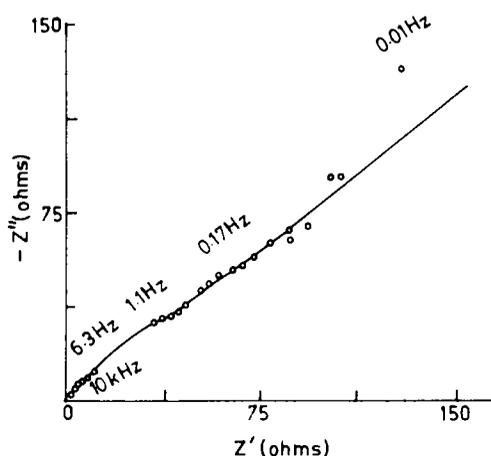


Figure 2. Impedance spectra for solid iron at -700 mV.

above 6.3 Hz, the impedance spectra bends and a small semi circle is obtained at high frequencies. This may be due to the ionisation of adsorbed hydrogen. The phase angle is found to have a constant value of 45° only in the frequency range of 10 to 100 Hz.

At $E = -700$ mV, a potential in the passive region, the impedance spectra exhibits a Warburg impedance beyond 6.3 Hz due to the diffusion of OH^- ions in the film (figure 2). The phase angle value is found to be 45° in the frequency range of 0.33 to 100 Hz.

The variation of $\log z$ with \log frequency gives the Bode plots (Gabrielli 1984). Bode plots for iron electrode at two different potentials of -1000 mV and -700 mV are presented (figure 3). At -1000 mV, the Bode plot is found to exhibit a linear segment with a slope of -2.5 in the frequency range of 0.1 to 10 Hz. The high frequency impedance is found to be 3 ohms which corresponds to solution resistance. At -1000 mV, the Bode plot reveals a linear segment with a slope of -2.7 in the range 0.5 to 1 Hz.

4.2 Porous iron

Figure 4 presents the impedance plot obtained for sintered porous iron electrode at -1000 mV. Below 1.1 Hz, a linear segment is obtained with a phase angle of $21 \pm 2.5^\circ$. The discontinuity between 1.1 to 6.3 Hz (joined by line) is observed due to resonating interaction of the test system with frequency response analyser. The capacitance value C is determined from the low frequency branch by its imaginary component at different frequencies. When the frequency decreases, the C value tends to increase, reaches a constant value of 769×10^{-3} F. The limiting value is attributed to the double layer capacitance on true electrode area. Resistivity value Ω is obtained both by extrapolation of low frequency branch towards the real axis and also from the Bode plot.

Figure 5 presents the complex plane impedance plot at -700 mV. The phase angle varies with frequency. In the frequency range 0.25 to 0.025 Hz a near constant value of 17° is observed. The impedance spectra in presence of additives is found to exhibit similar behaviour at -1000 mV and at -700 mV.

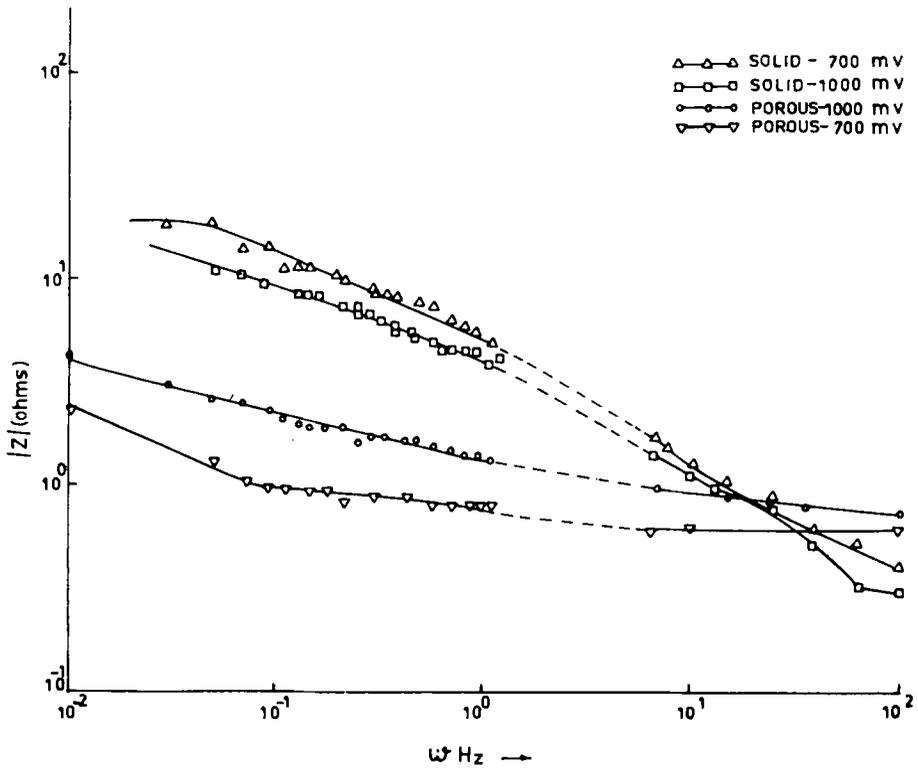


Figure 3. Bode plots for solid and porous iron electrodes.

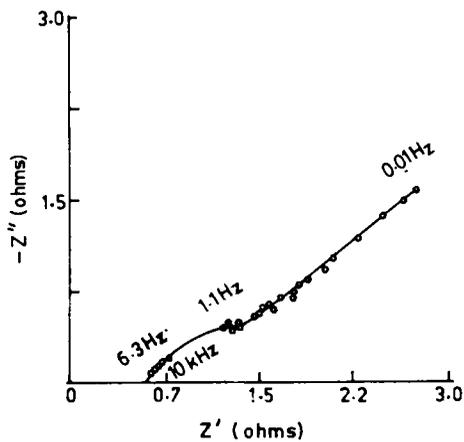


Figure 4. Impedance spectra for sintered iron electrode at -1000 mV.

5. Discussion

The iron electrode at -1000 mV may be understood as a surface covered by a partially oxidised hydrogen surface or as an oxide-free surface, while at -700 mV, the surface is completely covered with the passive film. At -700 mV, the ferrous ions emerging

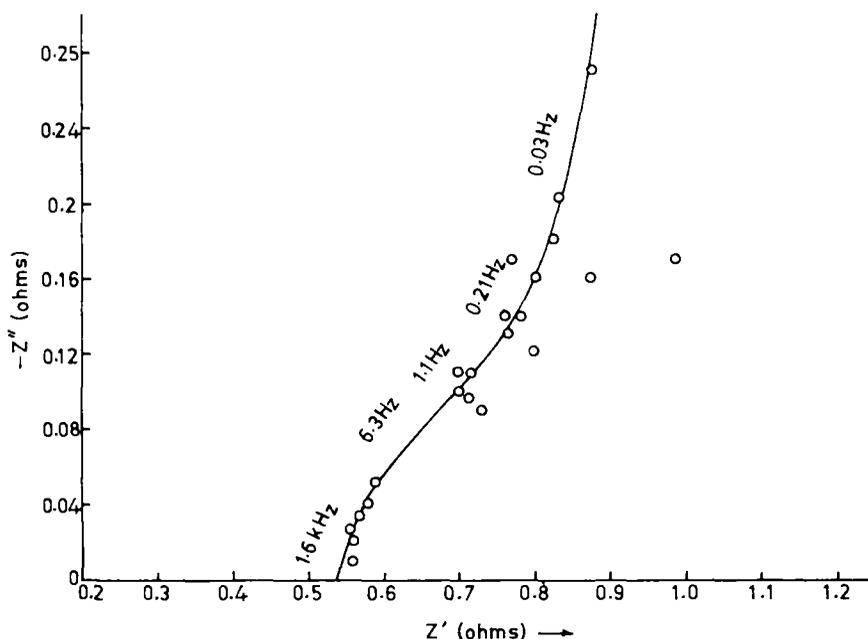
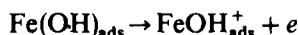
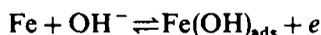


Figure 5. Impedance spectra for sintered iron electrode at -700 mV.

from the metal react with OH^- ions and settle on the electrode as a $\text{Fe}(\text{OH})_2$ film (Muralidharan and Veerashunmugamani 1985; Paruthimal Kalaiganan *et al* 1987).



In 6 M KOH solutions the dissolution of iron takes place as HFeO_2^- ions.

The porosity of an iron electrode plays an important role in deciding the cycle life of an alkaline Ni-Fe cell. Though other factors contribute to this aspect, the vital one is porosity. In case of insufficient initial porosity, the pores would be filled with $\text{Fe}(\text{OH})_2$ before all the iron could be filled whereas excessive initial porosity would lead to complete conversion of iron to iron hydroxide (Bryant 1970). Metal additives change the pore characteristics during discharge (Jayalakshmi and Muralidharan 1990).

For a porous electrode with semi-infinite pores, the phase angle of the impedance is of that of an equivalent solid planar electrode while the absolute magnitude of the impedance is proportional to the square root of the electrode impedance (Delevie 1967; Keiser *et al* 1976; Handy *et al* 1976). Hence a pure double layer capacitance leads to a phase angle of 45° and a purely diffusion controlled impedance to a phase angle of $45/2 = 22.5^\circ$.

The capacitance value C determined in the very low frequency domain corresponds to a solid planar electrode, while the high frequency domain relates to a cylindrical pore electrode. The double layer capacitance for solid electrodes at -1000 mV, determined in the frequency range of 10^2 to 10^4 Hz, is 346×10^{-6} F/cm². Using the

Table 1. Low frequency characteristics of porous electrodes.

| Electrode | - 1000 mV | | - 700 mV | |
|---------------|--------------------------------|--------------------------|---------------------------|--------------------------|
| | C_{dl} (mF/cm ²) | S (cm ² /g) | C (mF/cm ²) | S (cm ² /g) |
| Solid Fe | 0.346 | — | 0.346 | — |
| Porous Fe | 769 | 2222.5 | 1332 | 3849.7 |
| Fe + 1.8% Ag* | 1250 | 3612.7 | 1250 | 3612.7 |
| Fe + 0.82% Hg | 3330 | 9624.3 | 1200 | 3468.2 |
| Fe + 7.4% Cu | 2000 | 5780.3 | 1351 | 3904.6 |
| Fe + 10.9% S | 3330 | 9624.3 | 1204 | 3479.7 |
| Fe + 1.17% Pb | 1111 | 3210.9 | 1204 | 3479.7 |

*All additive quantities are w/w.

capacitance value for porous iron, the specific surface area S was calculated for porous iron electrodes and porous electrodes with metal additives (table 1).

Porous iron electrodes prepared from electrolytic iron powder with a specific surface area of 11.08 m²/g gave an S value of 0.238 m²/g.

It is customary in alkaline batteries to express energy density on the basis of the weight of the active material, and hence we prefer to express the surface area in terms of m²/g. The porosity was found to be 60 to 70% by the BET method (quantasorb using liquid N₂ and Hg penetration).

At - 700 mV, the capacitance value calculated for porous electrodes using the imaginary component of the impedance (0.25 to 0.025 Hz) gave a value of 1332 × 10⁻³ F. The apparent surface area calculated using C values for porous and solid electrodes is found to be 0.38 m²/g. This value obtained corresponds to a surface which is completely covered by Fe(OH)₂. A volume ratio of 1.72 of the film to the metal was also observed from the ratios of surface areas calculated at - 700 mV and - 1000 mV for porous iron.

When a porous electrode is considered (Candy and Fouillaix 1981) as a three-dimensional combination of small occluded pore units, the electrode impedances become very similar to that of a cylindrical pore electrode. If cylindrical pores are characterised by radius, r , length, l and number of pores, n , then at a frequency low enough for the electrode impedance to correspond to that of a planar electrode one can calculate, c and r values.

$$C = 2n\pi_e l C_{dl},$$

$$C/C_{dl} = S = 2n\pi r_e l,$$

$$r = (\rho \times l)/(3n\pi r_e^2).$$

The volume of the electrolyte inside pores V_e can be calculated by

$$V_e = n\pi r_e^2 l$$

If c , r and V_e are known experimentally, $r_e l$ and n can be determined.

$$r_e = \frac{2V_e C_{dl}}{C} = \frac{2V_e}{S},$$

$$l = (3r V_e/\rho)^{1/2},$$

$$n = S/(2\pi r_e l).$$

The average pore radius for the porous iron electrode at -1000 mV and -700 mV was estimated (table 2). The number of pores was calculated both at -1000 mV and at -700 mV (table 3). The frequency f_0 at which the penetration depth is equal to the pore length can be calculated.

$$\lambda = \frac{1}{2}(r_e/\rho\omega C_{dl})^{1/2},$$

where $W = 2\pi f$; for frequencies lower than f_0 the electrical signal penetrates the entire pore length and these values are given in table 4.

Table 2. Characteristics of pore: pore radius.

| Electrode | Radius (10^{-8} m) | | Change (%) |
|---------------|-----------------------|-----------|------------|
| | -1000 mV | -700 mV | |
| Porous Fe | 4.9 | 2.8 | -42.9 |
| Fe + 1.8% Ag* | 3.1 | 3.1 | — |
| Fe + 0.82% Hg | 1.2 | 3.2 | +2.5 |
| Fe + 7.4% Cu | 1.9 | 2.9 | +34.5 |
| Fe + 10.9% S | 1.1 | 3.0 | +63.3 |
| Fe + 1.17% Pb | 3.5 | 3.0 | -14.3 |

*All additive quantities are w/w; + increase; - decrease

Table 3. Characteristics of pores - total number of pores.

| Electrode | $n \times 10^8$ | | Change (%) |
|---------------|-----------------|-----------|------------|
| | -1000 mV | -700 mV | |
| Porous Fe | 5.7 | 1.72 | -69.8 |
| Fe + 1.8% Ag* | 13.6 | 13.6 | 0 |
| Fe + 0.82% Hg | 96.6 | 19.7 | -79.6 |
| Fe + 7.4% Cu | 37.8 | 16.9 | -55.3 |
| Fe + 10.9% S | 110 | 14.8 | -86.5 |
| Fe + 1.17% Pb | 11.2 | 14.8 | +24.3 |

*All additive quantities are w/w; + increase; - decrease

Table 4. Cylindrical pore dimensions.

| Electrode | Porosity (%) | V_e (cm^3) | l (cm) | | f_0 (mHz) | |
|---------------|--------------|-------------------------|------------|-----------|-------------|-----------|
| | | | -1000 mV | -700 mV | -1000 mV | -700 mV |
| Porous Fe | 68.9 | 0.0054 | 0.127 | 0.127 | 23 | 7.4 |
| Fe + 1.8% Ag* | 74.6 | 0.0058 | 0.132 | 0.132 | 8.3 | 8.3 |
| Fe + 0.82% Hg | 73.4 | 0.0057 | 0.132 | 0.132 | 1.2 | 9.1 |
| Fe + 7.4% Cu | 70.9 | 0.0055 | 0.128 | 0.128 | 33 | 7.0 |
| Fe + 10.9% S | 68.2 | 0.0053 | 0.126 | 0.126 | 1.2 | 9 |
| Fe + 1.17% Pb | 72.6 | 0.0057 | 0.130 | 0.130 | 9.8 | 9 |

*All additive quantities are w/w

5.1 Influence of additives

Small amounts of additives are always incorporated to increase battery life to act as depassivators, reduce gas evolution, improve conductivity and reduce self discharge. Copper and mercury are used to increase the hydrogen over-voltage (Linden 1984). Sulphur is incorporated to reduce the iron oxidation over-potential (Hordman 1972). Addition of Pb_2S to carbonyl iron gives a stable capacity (Lindstorm 1978).

At -1000 mV, the incorporation of foreign metal ions by cathodic deposition increases the surface area of the porous iron electrodes. In presence of Hg and S the surface area is highest. This may be due to the nature of the powdery deposit. At -700 mV, a near constant value of 0.34 ± 0.04 m²/g is observed for all electrodes indicating that the entire surface is covered by hydroxides.

The incorporation of Hg and S increase the number of pores at -700 mV, compared to the porous iron electrode. SEM studies have shown (Jayalakshmi and Muralidharan 1991) that mercury addition increased the inter particle neck growth and large definite voluminous pores were observed. This was due to the dissolution of iron as $HFeO_2^-$; Hg and S additions favour the dissolution of iron from the matrix causing an increase in number of pores. The reduction in the number of pores in the presence of Cu and lead is due to the stabilisation of the passive film of $Fe(OH)_2$ by them. The voluminous product closes the pores thereby causing a reduction.

At -1000 mV, the presence of additives increases the critical radius of the pores except in the case of lead. This suggests that dissolution of iron takes place in the mouth or the periphery of the pores and the dissolved $HFeO_2^-$ diffuses away from the pore. In presence of Pb supersaturation with respect to $HFeO_2^-$ ions is reached in the solution layer next to the electrode outside the pores and, as a result of the hydrolysis, these ions are deposited onto the electrode as $Fe(OH)_2$.

The length of the pores is unaffected at the two potentials studied. At -1000 mV the inclusions of Ag, Pb and Hg increase the length. This is reflected in the increase of the porosity of these electrodes. The f_0 values are found to decrease at -700 mV suggesting that the surface is covered by $Fe(OH)_2$ and that the additives have no effect (table 4).

5.2 m values

An analysis of the slope of a near linear segment in the Bode plots (m values) may throw some light on the nature of electrochemical processes. At -1000 mV, the presence of additives invariably increase the m value suggesting the enhanced resistance

Table 5. m values from Bode plot (10^{-1} – 10^2 Hz).

| Electrode | -1000 mV | -700 mV |
|---------------|------------|-----------|
| Porous Fe | -1.1 | -1.3 |
| Fe + 1.8% Ag* | -3.57 | — |
| Fe + 0.82% Hg | -3.43 | — |
| Fe + 7.4% Cu | -4.0 | -1.75 |
| Fe + 10.9% S | -4.25 | -0.8 |
| Fe + 1.17% Pb | -9.0 | -1.40 |

*All additive quantities are w/w

offered by these additives. At -700 mV, an average value of -1.0 ± 0.6 indicates a diffusion controlled phenomenon through the hydroxide film and the additives have no effect on the conductivity of the film (table 5).

6. Conclusions

In sintered porous iron electrodes, incorporation of foreign metal ions increases the surface area. Addition of Hg and S favours the dissolution of iron as HFeO_2^- from the matrix, thus increasing the number of pores; Cu and Pb stabilise the passive film and tend to close the pores.

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