269

Technical Update

Rechargeable alkaline iron electrodes

K. Vijayamohanan, T. S. Balasubramanian and **A. K. Shukla**
*Solid-state and Structural Chemistry Unit, Indian Institute of Science,
Bangalore - 560 012 (India)*

Abstract

In recent years, efforts have been made to produce efficient, porous, iron electrodes. Operational nickel/iron and iron/air batteries with substantially high power densities for motive-power applications have been developed. This article reviews pertinent literature on porous, iron electrodes and discusses directions for further avenues of research.

Introduction

Iron-electrode batteries, that could utilize virtually inexhaustible resources of iron, have been examined as futuristic electrochemical power sources [1–5]. Alkaline iron/air, and nickel/iron rechargeable batteries are two important systems [6–15].

The net cell reaction in a secondary nickel/iron cell is:

$$2NiOOH + 2H_2O + Fe \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2Ni(OH)_2 + Fe(OH)_2 \qquad (1)$$
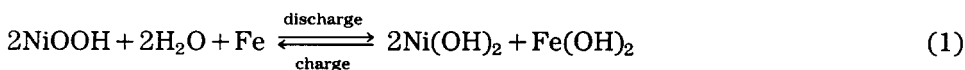
The system has an open-circuit voltage (OCV) of 1.33 V. Oxidation of active iron to $Fe(OH)_2$ comprises the first discharge step of the iron electrode. During subsequent discharge, conversion to Fe_3O_4 takes place. The cell reaction for a secondary iron/air cell, which has an OCV of 1.28 V, is:

$$Fe + \tfrac{1}{2}O_2 + H_2O \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Fe(OH)_2 \qquad (2)$$

The iron/air battery is especially attractive. It has a theoretical energy density value as high as 764 W h kg^{-1}. In practice, however, this performance has not been achievable. This is due to the low charge/discharge efficiencies of iron electrodes [2]. Another important scientific problem is the non-availability of an efficient rechargeable air electrode [16–18]. During recharge of an iron/air cell, the electrode reaction occurring at the air electrode is the anodic evolution of oxygen through the reaction:

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^- \tag{3}$$

At the high positive potential required for this reaction to proceed at a significant rate, undesirable side effects occur, viz., corrosion and/or erosion of the electrode support and poisoning of the electrocatalyst [19–21].

The charge/discharge cycle life of nickel/iron batteries under normal conditions of use is about 2000 cycles at 80% depth-of-discharge (DOD). This provides a long calendar life extending up to 20 years [3]. By comparison, typical lead/acid accumulators have much lower cycle lives with calendar life ranging from 3 to 6 years. A nickel/cadmium battery has a cycle life of about 1500 cycles at 80% DOD. Iron/air batteries under development are expected to exhibit a performance of close to 1000 cycles [3].

Iron electrodes also have safety and environmental advantages compared with other battery electrode materials such as nickel, cadmium, lead, and zinc, which are substantially toxic [22]. Furthermore, iron electrodes can withstand mechanical shocks and vibrations, as well as over-charge and deep-discharge.

Between 1910 and 1950, nickel/iron batteries were produced in large numbers in the U.S.A. and other countries for industrial traction applications. Further development and perfection of these batteries was, however, retarded by the emergence of the nickel/cadmium system. The latter has a lower degree of gas evolution and therefore less water-loss problems. Nickel/cadmium batteries have proved attractive for several applications, leading eventually to the present-day sealed, maintenance-free versions. In a parallel development, the advent of large-scale automobile manufacture, especially in the U.S.A. and Japan, stimulated the evolution of cost-effective lead/acid batteries. The situation has, however, changed since then. The limited resources, high cost, and toxicity of cadmium are such that the nickel/cadmium system will be almost certainly relegated to special applications that justify the extra investment, e.g., for service at sub-zero temperatures, in emergency power supplies, satellite power systems, and defence equipment. As for the lead/acid battery, its relatively poor cycle life, together with the high toxicity and corrosive effects of sulphuric acid vapours, point to the eventual preference for the nickel/iron counterpart. The latter is safe, economical and reliable in applications such as traction, lighting and fans in trains, shunting yard operations and mining locomotives. Nickel/iron and iron/air batteries have also been projected as potential candidates for electric vehicle (EV) applications ranging from family cars to commercial vans [23–28]. It is noteworthy that power densities generally required for EV applications (~ 100 W kg^{-1}) can be met by either of these battery systems (Table 1).

Problems that adversely affect the performance of iron electrodes are: spontaneous corrosion in the charged state (leading to a high rate of self-discharge), a low faradaic-efficiency for the anodic dissolution reaction, poor low-temperature performance, and low charge acceptance at high ambient temperatures due to a parasitic hydrogen evolution reaction (HER) [29–34]. In addition, the conventional 'Edison' process of electrode manufacture is

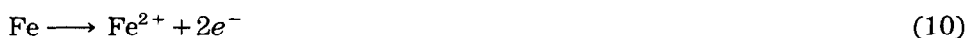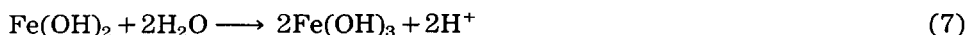TABLE 1

Nickel/iron and iron/air batteries

	Energy density (W h kg^{-1})	Power density (W kg^{-1})	Efficiency (%)	Cycle life
Current status				
Ni/Fe	50–60	75–110	60	1000
Fe/air	52–109	102–146	50	500
Projected status				
Ni/Fe	75–80	100–130	72	2000
Fe/air	98–195	181–309	68	1000

expensive [35]. Efforts have been made to circumvent these problems and it is strongly believed that iron-electrode batteries will attain commercial success in the near future [35–41].

Thermodynamic and electrochemical features of iron electrodes

Thermodynamic considerations

Iron is thermodynamically unstable in water and, hence, has a natural tendency to corrode. Various possible reactions for the iron/water system, as suggested by Latimer [42] and Pourbaix [43] are as follows:

$$H_2 \longrightarrow 2H^+ + 2e^- \tag{4}$$

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^- \tag{5}$$

$$Fe + 2H_2O \longrightarrow Fe(OH)_2 + 2H^+ + 2e^- \tag{6}$$

$$Fe(OH)_2 + 2H_2O \longrightarrow 2Fe(OH)_3 + 2H^+ \tag{7}$$

$$Fe^{2+} + 2H_2O \longrightarrow Fe(OH)_2 + 2H^+ \tag{8}$$

$$Fe(OH)_2 \longrightarrow HFeO_2^- + H^+ \tag{9}$$

$$Fe \longrightarrow Fe^{2+} + 2e^- \tag{10}$$

$$Fe + 2H_2O \longrightarrow HFeO_2^- + 3H^+ + 2e^- \tag{11}$$

$$Fe^{2+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ + e^- \tag{12}$$

$$HFeO_2^- + H_2O \longrightarrow Fe(OH)_3 + e^- \tag{13}$$

$$Fe(OH)_3 \longrightarrow FeO_2^- + H^+ + H_2O \tag{14}$$

$$HFeO_2^- \longrightarrow FeO_2^- + H^+ + e^- \tag{15}$$

These reactions have been employed to construct a Pourbaux (potential/ pH) diagram for the iron/water system, Fig. 1 [43, 44]. The region lying between 0.4 and -1.4 V versus the SHE, and corresponding to pH values above 14, is of interest for battery applications. The region of thermodynamic
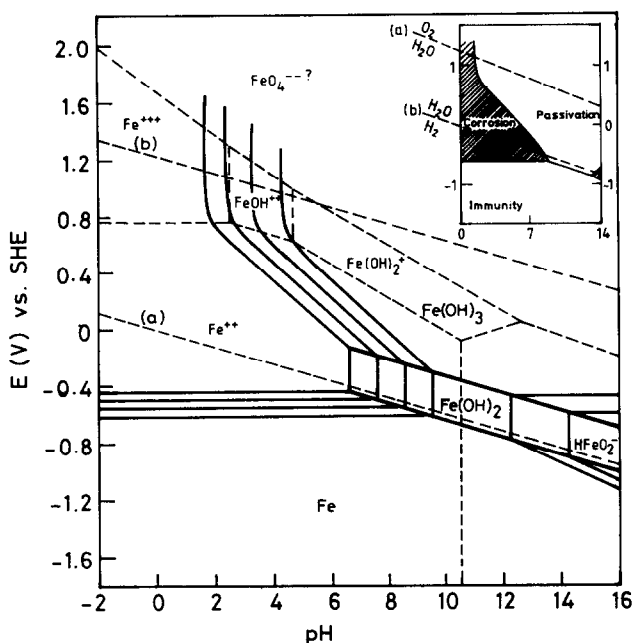
Fig. 1. Potential/pH diagram for Fe/H₂O system; inset shows regions of passivity, corrosion, and immunity.

stability for iron at standard temperature and pressure lies under line (a) (below -0.6 V versus SHE) with no part in common with water. Hydrogen evolution occurring as the conjugate reaction during the corrosion of iron can occur only below line (a). There are two nearly triangular regions for the corrosion of iron: one corresponding to Fe^{2+} and the other to $HFeO_2^-$. The iron electrode operation, however, only includes the corrosion domain of the latter. Deep discharge can shift the potential to a passive region where an oxide film can form [43]. Sufficient data exist on the thermodynamic characteristics of iron and its compounds [44–49]. The stability region for $Fe(OH)_2$ is well within the stability region of magnetite. $Fe(OH)_2$ is therefore thermodynamically unstable with regard to Fe_3O_4 and transforms to the latter through the reaction:

$$3Fe(OH)_2 \longrightarrow Fe_3O_4 + 2H_2O + H_2 \tag{16}$$

Several authors have considered the role of various iron species, present in solution, during charge/discharge reactions of iron electrodes via a dissolution/precipitation mechanism [31, 39, 50]. The poor low-temperature performance of iron electrodes, caused by variations in the concentrations of $HFeO_2^-$ and FeO_2^- ions, is substantiated by the thermodynamic data.

Double-layer and adsorption studies
   A few studies on the characteristics of the iron/alkali interface are available [51–56]. Measurements of differential capacity and potential decay

suggest the presence of significant quantities of adsorbed hydrogen on the electrode surface. The values of double-layer capacitance range between 320 and 420 μF cm^{-2} at low frequencies, but recede to 35 μF cm^{-2} at higher frequencies [55]. Such a large variation in capacitance has been attributed to slow ionization and discharge of adsorbed hydrogen. The capacitance values estimated recently from analysis of galvanostatic transients are about 150 μF cm^{-2} [51]. Various studies pertinent to the nature and properties of the iron/alkali interface are discussed below.

Adsorption at the iron/alkali interface
Changes in the kinetics, and the mechanism of iron electrode reactions in alkaline media, brought about by specific adsorption of ions, are important, as these could influence the extent of corrosion and passivation during the operation and maintenance of iron electrodes. Such aspects have been studied extensively and it is found that the adsorption of ions causes marked changes in the mechanism of both iron dissolution and the conjugate HER [52, 54–56].

Adsorption of hydrogen
Large quantities of adsorbed hydrogen on the surfaces of iron electrodes have been reported by several investigators [52, 56]. The frequency dependence of double-layer capacitance is attributed to this factor. Evidence for the adsorption of hydrogen has also been affirmed from impedance and potential-decay data.

Adsorption of oxygen
Adsorption of oxygen on iron electrodes to form a thin oxide layer is inevitable. According to Frumkin [57, 58], oxygen adsorption leads to a decrease in hydrogen overpotential and also helps to passivate iron electrodes in alkaline media.

Adsorption of sulphide ions
Adsorption effects of sulphide ions on iron electrodes have been widely investigated [52, 59–66]. The observed enhancement of the anodic process during discharge of iron electrodes has been ascribed to negative shifts in potential that result from the effects of adsorbed sulphide ions [63, 64]. Some investigators attribute the influence of sulphide ions to an increase in hydrogen overpotential. However, this contradicts the observed catalytic effects of sulphide ions towards the HER on iron in alkaline solutions [34, 36, 59, 64]. Thus, the exact role of sulphide ions in iron electrode reactions is not yet clearly understood [67].

Studies of the adsorption effects of various other ions on iron electrodes have also been conducted [36, 54, 63, 68–70]. Only a few organic compounds exhibit surface activity on iron electrodes. Such compounds are seldom studied since they are readily oxidized. Adsorption of cyanide ions has been investigated by impedance methods and it is found that they reduce the free surface available for HER [68].

Kinetics of iron electrode processes

Alkaline iron electrodes undergo several complex electrode processes during operation. Investigations reveal a variety of data about passivation, self-discharge, presence of intermediates, and formation of oxide films [2, 52, 70–76]. Various studies pertaining to these aspects are described below.

Galvanostatic charge/discharge studies

In the main, these studies include measurements on the capacity of electrodes during various charge/discharge cycles [30–37]. The capacity depends on factors such as charge/discharge rates, temperature, number of cycles, and electrolyte concentration. A typical charge/discharge curve for a porous, iron electrode along with the associated electrochemical steps is shown in Fig. 2. The theoretical capacity up to the first discharge step is 960 A h kg^{-1}. In practice, however, capacity values of 450–550 A h kg^{-1} with sintered, and 200–300 A h kg^{-1} with other types of electrodes, have been achieved [9–12, 76]. The capacity values usually stabilize after only a few cycles. This process is referred to technically as electrode 'formation'[77]. The capacity stabilisation subsequent to electrode formation is attributed to changes in conductivity, texture, and porosity of the active material [78].
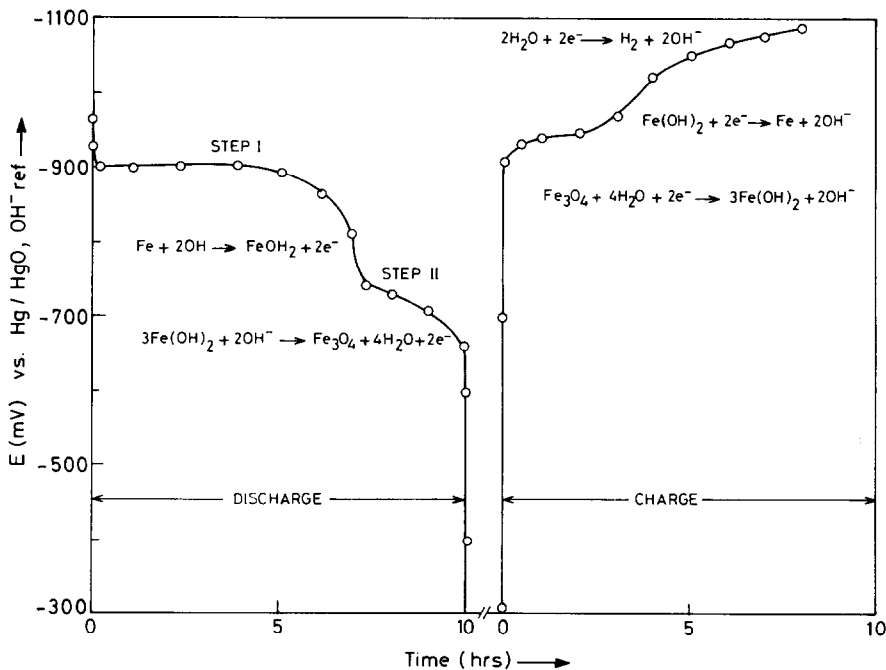
Fig. 2. A typical charge/discharge curve obtained for formed, pressed-plate, porous, iron electrode in 6 M KOH.

Variation in iron electrode capacity with charge/discharge rate has been reported by several investigators [2, 11, 12, 38]. High discharge rates facilitate the passivation of electrodes and prevent complete utilisation of the active material. On the other hand, iron electrodes undergo enhanced corrosion at low discharge rates. In both situations, a reduction in electrode capacity is inevitable. Charge/discharge studies at various rates show that the optimum rate varies with electrode morphology, as well as with temperature and electrolyte concentration [8]. In the case of sintered iron electrodes, the capacity reduces by 20% on doubling the discharge rate [2]. Studies reveal that the optimum capacity is achieved at a rate between $C/4$ and $C/6$ [10, 38].

a.c. Impedance studies

A few studies have been made on the a.c. impedance of porous, alkaline iron electrodes [55, 68]. Studies on pure iron wire electrodes have shown the presence of surface-adsorbed hydrogen [55]. Equivalent circuits have been analysed and the observed dispersion of capacitance and resistance data with frequency has been attributed to both non-homogeneity and the slow diffusion of hydrogen atoms over the electrode surface.

Voltammetric studies

Cyclic voltammetric investigations on alkaline iron electrodes have been widely reported [50, 65, 66, 78–85]. These establish the presence of intermediate species such as FeO_2^- and $HFeO_2^-$. Reaction schemes involving Fe, $Fe(OH)_2$, FeOOH, and Fe_3O_4 have also been discussed. In this context, the role of lithium ions in preventing passivation has been highlighted [79, 83]. The findings show that both the composition and the structure of the passive film, as well as the formation of Fe(II) and Fe(III) species, depend mainly on electrolyte composition, temperature, and additives [84–88].

Potentiodynamic studies conducted with stationary electrodes have resulted in the detection of various reaction species. Such experiments on iron electrodes corroborate the dissolution/precipitation mechanism for $Fe(OH)_2$ formation [81, 83]. Nevertheless, arguments regarding the negligible contribution of non-faradaic components to observed currents are still to be resolved. Equivalent studies conducted with stationary and rotating electrodes signify the importance of surface conditions that usually give rise to irreproducible data [89]. Potentiodynamic studies with sintered iron electrodes suggest that a high electrode porosity increases the separation between HER and $Fe(OH)_2$ reduction, and thereby causes a higher charge acceptance [37, 39]. The dissolution/precipitation mechanism is found to be operative, and the solubility of $HFeO_2^-$ ions is used to explain the variation of capacity with temperature. These studies are significant with regard to electrode kinetics, as are also investigations into electrolyte concentration and porosity variation in porous, alkaline iron electrodes. The effect of carbonate formation in the electrolyte has also been examined.
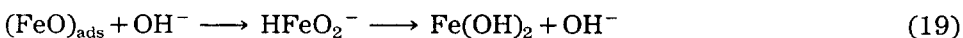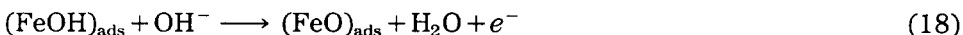
Transient studies

Anodic transients of alkaline iron electrodes have been examined quite extensively in order to derive the related kinetic parameters [72, 73, 90]. Some of these studies attribute the transient behaviour to compositional changes in the mixed-oxide layer due to diffusion of Fe(II) ions. The variation in behaviour of the electrodes is attributed to various impurity effects [54, 91]. An analysis of galvanostatic transients in cathodic and anodic directions in the linear polarisation regime shows that variations in resistance occurring inside the pores of an electrode with state-of-charge (SOC) could be appreciable during its operation [51].

Open-circuit decay transients at various SOCs have also been investigated for porous, alkaline iron electrodes [92, 93]. From these studies, it has been possible to arrive at a correlation between kinetic parameters and observed potential–recovery time constants. A diagnostic criterion for studying the effect of additives has also been suggested.

Most of the kinetic studies have been supplemented by various *in situ* and *ex situ* physical characterisation techniques such as X-ray diffraction [59, 94, 95], SEM [59, 96, 97], ellipsometry [98, 99], Mössbauer [100–103] and other spectroscopic [104–109] investigations.

Mechanism of iron electrode reactions

The percentage conversion of Fe to $Fe(OH)_2$ increases with alkali concentration [58, 110]. The overpotential remains invariant with change in KOH concentration but increases with current density. The Tafel slopes are about 0.04 V/decade at a current density of 10^{-6} A cm^{-2} [58]. Lower Tafel slopes are reported at lower current densities, indicating the probability of a different mechanism. A dissolution/precipitation mechanism involving $HFeO_2^-$ ions as intermediates in alkaline solutions is as follows:

$$Fe + OH^- \longrightarrow (FeOH)_{ads} + e^- \tag{17}$$

$$(FeOH)_{ads} + OH^- \longrightarrow (FeO)_{ads} + H_2O + e^- \tag{18}$$

$$(FeO)_{ads} + OH^- \longrightarrow HFeO_2^- \longrightarrow Fe(OH)_2 + OH^- \tag{19}$$

The formation of passive oxide is explained through the reaction:

$$(FeOH)_{ads} + OH^- \longrightarrow (FeOOH)_{ads} + H^+ + 2e^- \tag{20}$$
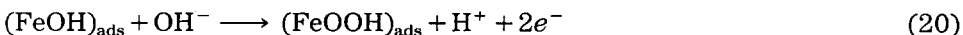
Different mechanisms have been proposed from studies conducted on smooth, iron electrodes [73, 90].

The formation of an $(FeOH)_{ads}$ surface intermediate has been established, and the presence of Fe(II) and Fe(III) species has been confirmed from ring/disc experiments [50, 54, 79, 90]. The mechanism has been described in detail using these intermediates [50, 61, 107, 111–117]. Research findings suggest that the first step of the charge/discharge reaction proceeds through dissolved intermediate $HFeO_2^-$ species whose concentration is strongly temperature-dependent. Other work shows [116–118] that the second step of the iron-electrode reaction proceeds via a solid-state mechanism.

Modelling of porous, iron electrodes

Electrode modelling provides suitable design criteria for the improvement of the charge/discharge performance of electrodes. The model should be based on fundamental processes occurring in the electrode, i.e., local and bulk mass-transfer, charge-transfer characteristics, and accompanying morphological changes. It should be noted that even macro-homogeneous models due to Newman and Tobias [119] and Micka [120], which are often employed satisfactorily, do not represent the complex dynamic behaviour of battery electrodes since several unrealistic assumptions are made, e.g., isotropic conductivity and one-dimensional electrical representation with uniform current distribution. Nevertheless, such models have been helpful in understanding various processes involving battery electrodes [121–127].

The only mathematical model that is available for porous, alkaline iron electrodes is a macro-homogeneous model [60]. Following a model for the magnetite film on carbon steel, a finite transmission analogue [128] has been employed to calculate the maximum capacity of an alkaline iron electrode [59, 129]. A large difference is observed between the experimental (46%) and calculated (76%) values of the porosities. This has been attributed to an over-simplification of the model, which neglects both electrode polarisation and passivation. The other major limitation of the model is that the large ohmic drop caused by discharge products is not included. Furthermore, electrode kinetic studies reveal that the electrode capacity depends on electrolyte concentration, and this factor is not accommodated in any of the models [60]. It should be pointed out that clogging of pores with $Fe(OH)_2$ alone cannot limit the capacity since $Fe(OH)_2$ is a gelatinous precipitate that allows the electrolyte to percolate through [58]. Furthermore, the conjecture that capacity is limited by the growth kinetics of $Fe(OH)_2$ film, and not by passivation, has not been validated. The role of impurities in affecting the growth kinetics of this film is equally ill-defined.

Self-discharge of iron electrodes

Extensive self-discharge is a major limitation of alkaline iron electrodes and it has been widely investigated [36, 40, 130–133]. The phenomenon is due to low hydrogen overpotential and a more cathodic reversible potential for iron dissolution in relation to the HER. Low hydrogen overpotential also causes the HER to compete with the reduction of $Fe(OH)_2$ to Fe. Losses in electrode capacity due to self-discharge increase with the stand time and SOC [36, 134]. Deluca [133] has reported a capacity loss of about 5% within 4 h, extending to 20% over 14 days, for fully charged iron electrodes.

Several techniques have been employed to investigate the self-discharge mechanism of iron electrodes [36, 40, 135–141]. Self-discharge of iron electrodes is a corrosion phenomenon that arises from the inherent thermodynamic instability of the Fe/H_2O system (Fig. 1). Ojefors [36] has explained

the increase in self-discharge rate with temperature in terms of the stability of $HFeO_2^-$ species.

During spontaneous dissolution of iron, the electrode gradually becomes coated with a film of $Fe(OH)_2$ as a result of the following corrosion reaction:

$$Fe \longrightarrow Fe^{2+} + 2e^- \tag{21}$$
$$2H_2O + 2e^- \longrightarrow 2OH^- + 2H_2 \tag{22}$$
$$\text{---}$$
$$Fe + 2H_2O \longrightarrow Fe(OH)_2 + H_2 \tag{23}$$

Fe^{2+} ions diffuse through the $Fe(OH)_2$ film under the influence of a concentration gradient and thus propagate film growth. Iofa [40] has explained the decrease in self-discharge rate with time in terms of the slowing down of Fe^{2+} diffusion with increase in film thickness. This, however, does not account for the variation of self-discharge rate with temperature and/or electrolyte concentration. Measurements on volumes of hydrogen evolved during self-discharge support the mixed-potential theory of corrosion for iron electrodes, with the HER as the cathodic conjugate reaction [2, 142].

Suppression of the HER during self-discharge can prevent loss of capacity. According to Frumkin [57], the presence of oxygen on the electrode surface leads to an increase in the overpotential for the HER which, in turn, could reduce self-discharge [143]. The method usually employed to increase the hydrogen overpotential is to incorporate certain additives into the electrode material that affect the kinetics of the associated electrode processes. The influence of various additives has been investigated by Ojefors [26]. It was found that although most of the additives did, indeed, decrease the self-discharge rate, an accompanying decrease also took place in the faradaic efficiency of the iron electrode reaction. This work did not, however, provide details on the mechanisms of the electrocatalytic effects brought about by the additives.

Electrode modifiers and electrolyte additives

The role of additives on the kinetics of iron electrode reactions is not yet clearly understood. The catalytic effects of Li^+ and S^{2-}-ions are well known but opinions regarding the mechanisms differ [36, 61, 131, 144–152]. Additives can be incorporated either in the active mass or in the electrolyte. The latter method has been used by Ojefors [36] for studying the self-discharge of sintered iron electrodes. Rozentvig [145] and Stepina and Iofa [61] have employed mechanical mixtures of additives with the active mass, but co-precipitation could be more effective.

Various additives have been found to bring about a decrease in the self-discharge rate (as stated above), an improvement in charge-retention and

discharge characteristics, an increase in capacity, and an improvement in cycle life and electrode stability. Additives are selected on the basis of the changes they effect on electrode structure, conductivity, and hydrogen overpotential. The composition and structure of the passive film also change with these additives and thereby facilitate (or retard) the diffusion of H^+, OH^- and Fe^{2+} ions. The mobilities of these ions are controlled by imperfections present in the electrode lattice.

Individual additives influence the electrode reactions differently, e.g., addition of Li^+ ions alters kinetic parameters such as apparent exchange current densities and transfer coefficients. According to Hampson et al. [112, 131], at low Li^+ concentration the structure of the oxide/solution interface is changed, causing hindrance to the HER. The bulk electrical conductivity of the electrode, as well as the rate of the HER, increase with the Li^+ ion concentration. Hills [134] is the first to have proposed a hindrance to oxide growth due to the presence of lithium, i.e., by a delay in the onset of passivity. Later, this claim was experimentally substantiated by Guzman et al. [79]. An analysis of electrodes subsequent to discharge showed the incorporation of only 1 wt.% of lithium.

The influence of sulphide ions has been studied in detail [34, 61, 65–67], and positive effects on the electrode performance have been explained using various models. Steady-state, galvanostatic, and potentiostatic polarisation studies conducted on sulphide-modified and sulphide-free iron electrodes, along with a phenomenological analysis in the linear polarisation regime, suggest that sulphide incorporation enhances bulk electrode conductivity [67].

Other additives that have been tested include: cations of Sb, Cd, Hg, Pb, Bi, La, Mn, Ca, Al, Co, Ni, Si, Zn and Mg metals; anions such as F^-, S_2^-, Se^{2-}, Cl^-, SiO_3^{2-} and $S_2O_3^{2-}$; molecules such as alizarin, tannin, silica gel, thiocarbamine, etc. [36, 66, 131, 145–153]. There are inconsistencies among the various studies. Some of the additives increase anodic passivation while others prevent it and help to stabilise the electrode capacity. The poisoning action of Mn and Ca is attributed to a close interaction of $Fe(OH)_2$ with these hydroxides, preventing its complete reduction to Fe.

A few investigators have claimed a total decrease in self-discharge with suitable additives, but the accompanying faradaic efficiencies are found to be low [29, 61]. It is believed that cations influence the structural features of the $Fe(OH)_2$ film by creating relative excess of positive charge around the Fe^{2+} ions in the lattice. The cations inhibit transfer of Fe^{2+} ions to interstices and thus increase the activation energy of the process. This, in turn, decreases the ionic conductivity and limits the anodic current. Adsorption of anions decreases the activation energy for the escape of Fe^{2+} ions due to a supplementary negative field. These explanations do not, however, account for the specificity of the additives. The latter should always be selected in such a manner that passivation is prevented and electrical conductivity is increased. In practice, the HER must be suppressed without sacrificing the faradaic efficiency of the iron electrode reaction.

Solid-state chemistry of iron electrodes

Phase composition, morphology, and crystallinity greatly influence the operational behaviour of iron electrodes. Changes in structure and volume of the active mass can influence the porosity, electrical conductivity, and

TABLE 2

Crystal chemistry data for various oxides and hydroxides of iron[a]

Species	Descriptions
α-Fe	Body centered cubic structure
Fe_3O_4 (magnetite)	Inverse spinel structure: $(Fe_8{}^{2+})_t(Fe_8{}^{2+}Fe_8{}^{3+})_oO_{32}{}^{2-}$.
α-FeOOH (goethite)	Hexagonal close packing with OH^- hydrogen bonded to O^{2-} ions; Fe^{3+} in o-sites.
β-FeOOH	Body centered cubic structure akin to α-MnO_2; Fe^{3+} in o-sites; stable only in the presence of certain interstitial impurities.
γ-FeOOH (lepidocrocite)	Cubic close packed structure with Fe^{3+} in o-sites; hydrogen bonding between OH^- ions.
δ-FeOOH	Hexagonal close packed structure with random distribution of Fe^{3+} on o-sites as in $Fe(OH)_2$; 20% of Fe^{3+} in t-sites.
$Fe(OH)_2$	Hexagonal close packed structure with Fe^{2+} in o-sites as in $Mg(OH)_2$ lattice.

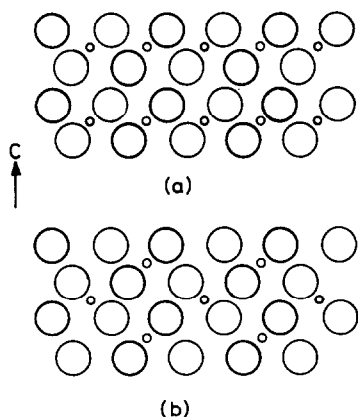[a]o and t represent octahedral and tetrahedral sites, respectively.

Fig. 3. Comparison of structures of discharge products of alkaline iron electrode: (a) $Fe(OH)_2$; (b) δ-FeOOH.

mechanical strength of the electrodes [154, 155]. An understanding of the interplay of various solid-state parameters is therefore vital. Uniformly dispersed grains of active mass are preferable *vis-à-vis* agglomerated lumps. The changes in lattice parameters should not be large for the phases. Furthermore, a change in the orientation of the various crystallites can also influence electrode performance.

The crystal chemistry data for Fe, Fe_3O_4, $Fe(OH)_2$, and FeOOH (Table 2) are useful to account for structural changes accompanying the operation of iron electrodes. During discharge of the iron electrode, the b.c.c. iron lattice changes to $Fe(OH)_2$; the latter has a CdI_2-type layered structure [156–158]. The subsequent conversion to FeOOH on further discharge is structurally feasible, as shown in Fig. 3.

Conclusions

From the above discussion, it is clear that rechargeable iron electrodes could have long cycle-life, even under deep-discharge conditions. The electrodes are inherently rugged and can withstand severe mechanical and electrochemical abuse. Furthermore, an appraisal of cost, life, performance, and environmental safety supports the commercial viability of iron-based batteries. It is imperative, however, to conduct further research in order to unravel the mechanisms responsible for passivation/self-discharge of iron electrodes and thus to discover means to restrain the associated deleterious effects.

Acknowledgements

References

1 M. A. Klochko and E. J. Casey, *J. Power Sources*, 2 (1977/78) 201.
2 L. Ojefors, *Studies on Alkaline Iron Electrodes*, Swedish National Development Co., Royal Institute of Technology, Stockholm, 1975.
3 S. Sathyanarayana, *Nickel–Iron Storage Batteries*, A status report & techno-economic survey for India, National Research Development Co., 1983.
4 Research, development and demonstration of nickel–iron battery for electric vehicle propulsion, *Annu. Status Rep. for FY '82, 31-109-38, 4141-*, Westinghouse Electric Corporation, Pittsburgh, 1982.
5 K. S. Hardy and R. S. Kirk, *Proc. 20th Intersoc. Energy Conv. Eng. Conf.*, Vol. I, 1985, p. 705.
6 F. G. Will, in B. D. McNicol and D. A. J. Rand (eds.), *Power Sources for Electric Vehicles*, Elsevier, Amsterdam/New York, 1984.

7 J. Labat, *Prog. Batteries Solar Cells, 6* (1987) 236.
8 W. A. Bryant, *Electrochim. Acta, 24* (1979) 1057.
9 A. Gibney and D. Zuckerbroad, in J. Thomson (ed.), *Power Sources 9*, Academic Press, London, 1982, p. 143.
10 K. W. Lexov, G. Kramer and V. A. Oliapuram, in J. Thomson (ed.), *Power Sources 8*, Academic Press, London, 1981, p. 389.
11 B. Anderson, L. Ojefors and R. Hudson, in J. Thomson (ed.), *Power Sources 8*, Academic Press, London, 1981, p. 379.
12 H. Cnobloch, D. Groppel, D. Kuhl, W. Nippe and G. Siemesen, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 261.
13 W. A. Bryant, C. T. Liu and E. S. Buzzelli, *Proc. 28th Power Sources Symp.*, PSC Cttee., NJ, 1978, p. 152.
14 B. Anderson and L. Ojefors, in J. Thomson (ed.), *Power Sources 7*, Academic Press, London, 1979, p. 329.
15 H. Cnobloch, D. Groppel, W. Nippe and F. von Sturm, *Chem.-Ing.-Tech., 45* (1973) 203.
16 L. Ojefors and L. Carlsson, *J. Power Sources, 2* (1977/78) 287.
17 M. Bursell, in J. Thomson (ed.), *Power Sources 8*, Academic Press, London, 1981, p. 513.
18 D. A. J. Rand, *J. Power Sources, 4* (1979) 101.
19 A. M. Kannan, A. K. Shukla and S. Sathyanarayana, *J. Power Sources, 25* (1989) 141.
20 L. Carlsson and L. Ojefors, *J. Electrochem. Soc., 127* (1980) 525.
21 A. M. Kannan, A. K. Shukla and S. Sathyanarayana, *J. Electroanal. Chem., 281* (1990) 339.
22 M. Sittig, *Hazardous and Toxic Effects of Industrial Chemicals*, Noyes Data Corp., 1979.
23 M. Cenek, J. Kazelle and B. Wilczek, in *Int. Symp. Mechanization and Automation in Chemical Power Sources Production, Oct. 11–13, 1988, Poznan, Poland.*
24 B. I. Uginov, in *Int. Symp. Mechanisation and Automation in Chemical Power Sources Production, Oct. 11–13, 1988, Poznan, Poland.*
25 T. Mitsumata, K. Takahasi, E. Kitamara and T. Iwaki, *Denki Kagaku, 53* (1985) 417.
26 K. S. Hardy and J. M. Langendoen, Advanced Vehicle System Concepts,,, *IEEE Trans. Veh. Technol., V7.32* (1) Feb., 1983.
27 K. S. Hardy and V. P. Roan, SAE paper no. 850223, Advanced vehicle technology assessment, *SAE Int. Cong. Exposition, Detroit, Michigan, U.S.A., Feb., 1985.*
28 W. H. Deluca, A. F. Tummillo, P. L. Diwer and N. P. Yao, paper EVC no. 8301, *Electric Vehicle Council Symp. and Expo VII, Dearborn, MI, U.S.A., Oct., 1983.*
29 O. Lindstrom, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 283.
30 S. Hills and A. J. Salkind, *Proc. 22nd Power Sources Symp.*, PSC Committee, NJ, U.S.A., 1968, p. 66.
31 L. Ojefors, *J. Electrochem. Soc., 123* (1976) 1139.
32 H. N. Sieger, *Proc. 16th Intersoc. Energy Conv. Eng. Conf.*, Vol. II, 1982, p. 102.
33 R. Bonnaterre, R. Doisnean, M. C. Petit and J. P. Stervinon, in J. Thomson (ed.), *Power Sources 7*, Academic Press, London, 1978, p. 249.
34 P. R. Vassie and A. C. C. Tseung, *Electrochim. Acta, 21* (1976) 299.
35 S. U. Falk and A. J. Salkind, *Alkaline Storage Batteries*, Wiley, New York, 1964, pp. 89–104.
36 L. Ojefors, *Electrochim. Acta, 21* (1976) 263.
37 B. Anderson and L. Ojefors, *J. Electrochem. Soc., 123* (1976) 824.
38 E. R. Bowerman, *Proc. 22nd Power Sources Conf.*, PSC Committe, NJ, U.S.A., 1968, p. 70.
39 J. Labat, J. C. Jarrousseiu and J. F. Lauret, in J. Thomson (ed.), *Power Sources 5*, Academic Press, London, 1970.
40 Z. A. Iofa, *Zh. Prikl. Khim., 56* (1983) 1164.
41 T. Iwaki, T. Mitsumata and H. Ogawa, *Prog. Batteries Solar Cells, 4* (1982) 255.
42 W. M. Latimer, *Oxidation Potentials*, Prentice-Hall, Englewood Cliffs, NJ, U.S.A., 1961.

43 M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, London, 1966.
44 M. Pourbaix, *Corros. Sci.*, *12* (1972) 161.
45 I. A. Dibrov, B. I. Uzhinov, T. V. Grigoreva and M. N. Mashevich, *Zh. Prikl. Khim.*, *51* (1978) 1954.
46 I. A. Dibrov, S. M. Chervyak-Voronich, T. V. Grigoreva and G. M. Kozlova, *Elektrokhimiya*, *16* (1980) 786.
47 T. Markovic and Z. Pavlovic, *Monatsh. Chem.*, *95* (1964) 74, 78.
48 Ya. Sapozhnikova and E. M. Rozenblat, *Elektrokhimiya*, *10* (1974) 1281.
49 S. J. Lenhart, *Proc. 16th Intersoc. Energy Conv. Eng. Conf.*, Vol. I, 1981, p. 663.
50 R. D. Armstrong and I. Baurhoo, *J. Electroanal. Chem.*, *34* (1972) 41, 325.
51 K. Vijayamohanan, A. K. Shukla and S. Sathyanarayana, *J. Electroanal Chem.*, *295* (1990) 59.
52 S. Yu Volosova, A. Z. Iofa and T. G. Stepina, *Elektrokhimiya*, *13* (1977) 393.
53 A. P. Pyankova and Z. A. Iofa, *Elektrokhimiya*, *10* (1974) 1344.
54 E. J. Kelly, *J. Electrochem. Soc.*, *115* (1968) 1111.
55 B. V. Batrakov and Z. A. Iofa, *Elektrokhimiya*, *20* (1965) 123.
56 S. P. Shavkunov, I. N. Shertobitova and V. V. Kuznetsov, *Eleketrokhimiya*, *19* (1983) 549, 706.
57 A. N. Frumkin, *Discuss. Faraday Soc.*, *1* (1946) 57.
58 B. Kabanov, R. Burstein and A. N. Frumkin, *Discuss. Faraday Soc.*, *1* (1946) 259.
59 C. S. Tong, S. D. Wang, U. U. Wang and C. T. Wang, *J. Electrochem. Soc.*, *129* (1982) 1173.
60 K. Micka and I. Roussar, *Eleketrochim. Acta*, *29* (1984) 1411.
61 T. G. Stepina and Z. A. Iofa, *Elektrokhimiya*, *16* (1980) 888.
62 K. Micka and Z. Zabransky, *J. Power Sources*, *19* (1987) 315.
63 S. A. Rozentiveig and Z. V. Shcherbakova, *Zh. Fiz. Khim.*, *35* (1961) 2547.
64 V. P. Balyaev, V. I. Aeteme'v and A. M. Sukhotin, *Zashch. Met.*, *21* (1984) 403.
65 G. Berger and F. Haschka, in L. J. Pearce (ed.), *Power Sources 11*, Taylor and Francis, Hampshire, U.K., 1986, p. 237.
66 J. Cerny and K. Micka, *J. Power Sources*, *25* (1989) 111.
67 K. Vijayamohanan, A. K. Shukla and S. Sathyanarayana, *J. Electroanal. Chem.*, *289* (1990) 55.
68 S. P. Shavkunov, I. N. Sherstobitov and V. V. Kuznetsov, *Elektrokhimiya*, *19* (1983) 816.
69 V. E. Past and Z. A. Iofa, *Zh. Fiz. Khim.*, *33* (1959) 1230.
70 A. Pyankova, V. V. Batrakova and Z. A. Iofa, *Elektrokhimiya*, *2* (1960) 1000.
71 F. Foerster, *Z. Elektrochem.*, *16* (1910) 461.
72 T. Hurlen, *Electrochim. Acta*, *8* (1963) 609.
73 J. O'M. Bockris and H. Kita, *J. Electrochem. Soc.*, *108* (1961) 676.
74 P. Lorbeer and W. J. Lorenz, *Corros. Sci.*, *21* (1981) 79.
75 A. J. Salkind, C. J. Venuto and S. U. Falk, *J. Electrochem. Soc.*, *111* (1964) 493.
76 W. A. Bryant, *J. Electrochem. Soc.*, *126* (1979) 1899.
77 K. Vijayamohanan, A. K. Shukla and S. Sathyanarayana, *Indian J. Technol.*, *24* (1986) 436.
78 K. Vijayamohanan, A. K. Shukla and S. Sathyanarayana, *J. Power Sources*, *32* (1990) 329.
79 R. S. Guzman, J. R. Vilche and A. J. Arvia, *Electrochim. Acta*, *11* (1981) 551.
80 G. P. Kalaignan, V. S. Muralidharan and K. I. Vasu, *J. Appl. Electrochem.*, *17* (1987) 1083.
81 R. S. Guzman, J. R. Vilche and A. J. Arvia, *Elektrochim. Acta*, *24* (1979) 395.
82 D. Geana, A. A. El Miligy and W. J. Lorenz, *J. Appl. Electrochem.*, *4* (1974) 337.
83 R. S. Guzman, J. R. Vilche and A. J. Arvia, *J. Appl. Electrochem.*, *11* (1981) 55.
84 A. Wieckowski and E. Ghali, *Electrochim. Acta*, *30* (1985) 1423.
85 V. S. Muralidharan and V. Veerashanmugan, *J. Appl. Electrochem.*, *15* (1985) 675.
86 F. Beck, R. Kous and M. Oberst, *Electrochim. Acta*, *30* (1985) 173.
87 G. J. Bignold, *Corros. Sci.*, *12* (1972) 145.

88 A. L. Rotinyan and I. A. Shoshina, *Zh. Prikl. Khim.*, *59* (1986) 2309.
89 G. S. Aleksandrova, I. A. Shoshina, T. V. Subbotina, V. M. Fantgof and A. L. Rotinyan, *Zh. Prikl. Khim.*, *56* (1983) 1540.
90 S. Asakura and K. Nobe, *J. Electrochem. Soc.*, *118* (1971) 136.
91 C. M. Shepherd and S. Schuldiner, *J. Electrochem. Soc.*, *115* (1968) 1124.
92 K. Vijayamohanan, A. K. Shukla and S. Sathyanarayana, *J. Power Sources*, *21* (1987) 53.
93 K. Vijayamohanan, A. K. Shukla and S. Sathyanarayana, *Electrochim. Acta*, *36* (1991) 369.
94 H. G. Silver and E. Lekas, *J. Electrochem. Soc.*, *117* (1970) 5.
95 V. M. Fantgof and L. M. Lishanski, *Elektrokhimiya*, *18* (1982) 571, 574, 647.
96 L. Ojefors, *J. Electrochem. Soc.*, *123* (1976) 1691.
97 E. N. Leschcheava, T. K. Teplinskaya, I. A. Aguf and K. M. Soloveya, *Zh. Prikl. Khim.*, *59* (1985) 1034.
98 T. G. Stepina, A. Z. Iofa, E. V. Kosatkin, V. A. Shepelin and V. A. Safonov, *Elektrokhimiya*, *16* (1980) 1884.
99 T. K. Teplinskaya, N. N. Fedorova and S. A. Rozentsveig, *Zh. Fiz. Khim.*, *38* (1964) 2176.
100 A. M. Pritchard and B. J. Mould, *Corros. Sci.*, *119* (1971) 1.
101 Y. Geronov, I. Tomov and S. Georgiev, *J. Appl. Electrochem.*, *5* (1975) 351.
102 D. A. Corrigan, R. S. Conell, C. A. Fierro and A. Scherson, *J. Phys. Chem.*, *91* (1987) 5009.
103 C. Fierro, R. E. Carbonio, D. Scherson and E. B. Yeager, *J. Phys. Chem.*, *91* (1987) 6579.
104 D. A. Harrington, A. Wieckowski, S. D. Rosasco, B. C. Scharolt, G. N. Salaita and A. T. Hubbard, *Corros. Sci.*, *25* (1985) 849.
105 D. A. Harrington, A. Wieckowski, S. D. Rosasco, G. N. Salaita and A. T. Hubbard, *Langmuir*, *1* (1985) 232.
106 J. Olifjord, *J. Appl. Electrochem.*, *5* (1975) 145.
107 H. Neugebauer, G. Nauer, N. Birendakonopiz and G. Gidali, *J. Electroanal. Chem.*, *122* (1981) 381.
108 J. O'M. Bockris, *Corros. Sci.*, *29* (1989) 291.
109 P. M. A. Sherwood, *Chem. Soc. Rev.*, *85* (1985) 1.
110 B. Ershler, *Acta Physicochim. URSS*, *19* (1944) 139.
111 I. A. Ammar, *Corros. Sci.*, *17* (1977) 583.
112 N. A. Hampson, R. J. Latham, A. Marshall and R. D. Giles, *Electrochim. Acta*, *19* (1974) 397.
113 K. M. Gorbunova and L. I. Liamina, *Electrochim. Acta*, *11* (1966) 457.
114 A. P. Pyankova and Z. A. Iofa, *Zh. Prikl. Khim.*, *46* (1973) 529.
115 D. M. Drazic and C. S. Hao, *Electrochim. Acta*, *27* (1982) 1409.
116 V. S. Flerov and L. T. Pavlova, *Elektrokhimiya*, *3* (1967) 621.
117 I. N. Sherstobikova, B. N. Kabanov and D. I. Leikis, *Elektrokhimia*, *4* (1968) 1228.
118 V. N. Flerov, L. I. Pavlova and L. V. Uzinger, *Zh. Prikl. Khim.*, *38* (1965) 569.
119 J. Newman and C. Tobias, *J. Electrochem. Soc.*, *109* (1962) 1183.
120 K. Micka, *Collect. Czech. Chem. Commun.*, *29* (1964) 1998.
121 K. J. Euler, *Electrochim. Acta*, *18* (1973) 385.
122 D. Simonsson, *J. Appl. Electrochem.*, *4* (1974) 109.
123 K. Micka and L. Rousar, *Electrochim. Acta*, *18* (1973) 629.
124 A. Winsel, *Chem.-Ing.-Tech.*, *43* (1973) 191.
125 R. de Levie in P. Delahay (ed.), *Adv. Electrochem. Electrochem. Eng.*, *6* (1967) 329.
126 W. Tiedemann and J. Newman, *J. Electrochem. Soc.*, *122* (1975) 1482.
127 J. Newman and W. Tiedemann, *AIChE J.*, *21* (1975) 25.
128 Y. S. Park and D. D. McDonald, *Corros. Sci.*, *23* (1983) 295.
129 P. Selanger, *J. Appl. Electrochem.*, *4* (1974) 263.
130 P. Hersh, *Trans. Faraday Soc.*, *51* (1955) 1442.

131 N. A. Hampson, R. J. Latham, A. N. Oliver, R. D. Giles and P. C. Jones, *J. Appl. Electrochem.*, *3* (1973) 61.
132 V. J. Linnerbom, *J. Electrochem. Soc.*, *105* (1958) 322.
133 W. H. Deluca, *16th Intersoc. Energy Conv. Eng. Conf.*, Vol. 2, 1981, p. 773.
134 S. Hills, *J. Electrochem. Soc.*, *112* (1966) 1048.
135 J. O'M. Bockris, J. McBreen and L. Nanis, *J. Electrochem. Soc.*, *112* (1965) 1025.
136 T. S. Lee, *J. Electrochem. Soc.*, *118* (1971) 1278.
137 R. Carta, S. Dernini, A. M. Polcaro, P. F. Ricci and G. Tola, *J. Electroanal. Chem.*, *257* (1988) 257.
138 R. N. O'Brien and P. Seto, *J. Electrochem. Soc.*, *117* (1970) 32.
139 A. P. Pyankova, B. V. Batrakov and Z. A. Iofa, *Elektrokhimiya*, *2* (1966) 1000.
140 Z. A. Iofa, A. P. Pyankova and G. V. Pankina, *Zh. Prikl. Khim.*, *56* (1983) 1067.
141 Y. K. Tamm, P. M. Vares and V. E. Past, *Elektrokhimiya*, *24* (1988) 402.
142 I. A. Shoshina, G. S. Aleksandrova, A. L. Rotinyan and A. N. Nefedov, *Elektrokhimiya*, *21* (1985) 1552.
143 E. M. Kuchinski and I. E. Vaselovskiya, *Proc. 4th Conf. Electrochemistry*, Vol. 3, Consultants Bureau, NY, 1961.
144 E. Ya. Sapozhnikova and E. M. Roizenblat, *Elektrokhimiya*, *10* (1974) 1281.
145 S. A. Rozentsveig and V. I. Levina, *Proc. 4th Conf. Electrochemistry*, Vol. 2, Consultants Bureau, NY, 1961.
146 R. C. Salvarezza, H. A. Videla and A. J. Arvia, *Corros. Sci.*, *22* (1982) 815.
147 D. W. Shoesmith, P. Taylor, M. G. Bailey and B. Ikeda, *Electrochim. Acta*, *23* (1978) 903.
148 D. S. Poa, J. F. Miller and N. P. Yao, *Tech. Rep. ANL/OEPM-85-2*, Argonne National Laboratory, 1985.
149 W. Lorenz, *Angew. Chem.*, *66* (1954) 591.
150 E. N. Leshcheva and T. K. Teplinskaya, *Zh. Prikl. Khim.*, *59* (1986) 1113.
151 E. B. Eronko, A. V. Bogdanov, I. A. Shoshina and T. K. Teplinskaya, *Zh. Prikl. Khim.*, *59* (1986) 1011.
152 T. Mitsumata and T. Iwaki, *Denki Kagaku*, *53* (1985) 413.
153 O. Lindstrom, *U.S. Patent No. 4 078 120* (Mar. 7, 1978).
154 A. L. Mackay, in J. H. de Boer (ed.), *Proc. 4th Int. Symp. Reactivity of Solids*, 1960.
155 A. M. Novakovskii, S. A. Grushkina and R. L. Kozlova, *Zh. Prikl. Khim.*, *46* (1973) 2150, 2183.
156 A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, London, 1970.
157 S. Okamoto, *J. Am. Ceram. Soc.*, *51* (1968) 594.
158 M. B. Strauss and M. C. Bloom, *J. Electrochem. Soc.*, *107* (1960) 73.