Some Electrochemical Aspects of the Becher Process

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I declare that this thesis is my own account of my research and contains as its main content work which has not been previously submitted for a degree at any tertiary institution.

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Abstract

The Becher process is used to upgrade ilmenite (~60% TiO_2) to synthetic rutile (92-95% TiO_2). Reduced ilmenite ($FeTiO_2$) is an intermediate mineral product and the industrial process whereby metallic iron is corroded from the TiO_2 matrix (leaving synthetic rutile) using air and ammonium chloride solutions is termed aeration. This thesis is concerned with the electrochemistry of the corrosion reaction that is the heart of this aeration step.

Synthetic rutile is almost exclusively used as a feedstock for the chloride process which produces pigment grade TiO_2. The Becher process is but one a number of processes that produce feedstocks for the chloride process. Together with the Becher process, these alternative processes are briefly reviewed in Chapter 1 followed by a detailed review of the Becher aeration step. Also included in Chapter 1 is a brief review of the thermodynamics for the iron-water system and, following a literature review on ferrous-ammine chemistry, a new Eh-pH diagram for the iron-water-ammonia system is presented using recently published data.

The investigation of the electrochemistry of anodic iron dissolution in Chapter 3 reveals some interesting results about the influence of aqueous NH_4Cl. An air-formed film only a few monolayers thick (9-18 Å) passivates iron after surface preparation. Ammonium ion is responsible for the rapid removal of this film after immersion which then allows fast active dissolution to occur upon anodic polarisation. Without ammonium ion the air-formed film passivates the iron during polarisation. Ammonium ion also increases the active dissolution current density while chloride inhibits active dissolution. However, chloride is responsible for breaking down the air- and anodically-formed films at relatively high anodic potentials. The activation energy for anodic iron dissolution in 0.2 M NH_4Cl up to 150°C is reported.

In Chapter 4 it is shown that oxygen is reduced on iron via a 4-electron mechanism in air-saturated 0.2 M NH_4Cl and that reduction is diffusion controlled. On gold, every oxygen molecule requires between 0 and 4 electrons depending on the potential. The oxygen reduction current density is proportional to the oxygen partial pressure up to 300 kPa. At 300 kPa oxygen partial pressure, the current density nearly doubled between 80 and 130°C due to the combination of three different effects.

In Chapter 5 it is shown that in air-saturated 0.2 M NH_4Cl the air-formed film inhibits iron corrosion for the first 20 to 30 minutes but then is removed allowing iron to

corrode quickly and uniformly. γ-FeOOH forms continuously as a porous film adhering to the surface and begins to inhibit corrosion only after 3 hours immersion. Ammonium ion is necessary for the removal of the air-formed film while chloride alone results in the localised breakdown of the film leading to pitting corrosion. However, above pH 7.5, the air-formed film is stable even in the presence of ammonium ion and, in the presence of chloride, pitting corrosion also results. Even though iron corrosion is essentially oxygen diffusion controlled at ambient pressures, the corrosion rate is not proportional to the oxygen partial pressure due to the formation of a thick γ-FeOOH film. Increasing the temperature to above 80°C increases the corrosion rate at high pressure largely due to solubilisation of the thick film.

A novel application of the carbon paste electrode technique to the investigation of the electrochemistry of anodic iron dissolution from whole reduced ilmenite grains is described in Chapter 6. Anodic dissolution is potential dependent but strongly limited by an air-formed passive film. Ammonium ions do not assist in the removal of this film; rather, chloride ions were found to increase the anodic current density by assisting in the breakdown of the air-formed passive film. Also presented in this Chapter is some preliminary evidence linking the variability of the aeration time with the stability of the air-formed film: the less stable the air-formed film, the shorter the aeration time.

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List of Symbols

Symbol	Meaning
ω	Angular frequency, rad s^{-1}. Where $\omega = 2\pi f$
τ	time constant, s
σ	Warburg diffusion coefficient, Ω s$^{-0.5}$
β	Cumulative formation constant
υ	Potential sweep rate, mV s^{-1}
B	Composite Tafel parameter, V
b_a	Anodic Tafel parameter, V
b_c	Cathodic Tafel parameter, V
C_b	Bulk dissolved oxygen concentration, mol cm^{-3}
C_{dl}	Double layer capacitance, F cm^{-2}
C_i	Molarity of species i, M
ΔE	Alternating current excitation voltage, V
D	Diffusion coefficient, cm^2 s^{-1}
E	Overpotential, V
E_a	Activation energy, kJ mol^{-1}
E_{corr}	Corrosion potential, V
E_p	Peak potential, V
E_{Ra}	Anodic reversal potential, V
E_{Rc}	Cathodic reversal potential, V
f	Frequency, Hz
F	Faraday constant, 96485 C
Fe_M	Metallic iron content
Fe_T	Total iron content
H	Henry's law constant, kPa
i	Total current density, A cm^{-2}
i_{corr}	Corrosion current density, A cm^{-2}
i_k	Activation controlled current density, A cm^{-2}
i_l	Diffusion limited current density, A cm^{-2}

List of Symbols (continued)

Symbol	Meaning
I_p	Peak current density, A cm^{-2}, mA cm^{-2}
j	$\sqrt{-1}$
k	Rate constant, m s^{-1}
K_i	Solubility constant for species i
mpy	mils per year (corrosion rate)
$|Z|$	Modulus of impedance Z_f, Ω cm^2
α	Constant phase element
n	Number of electrons
ν	Kinematic viscosity, cm^2 s^{-1}
p_g	Gas partial pressure, kPa
Q_a	Anodic charge, C
Q_c	Cathodic charge, C
RC	Resistor-capacitor parallel couple
R_{Me}	Polarisation resistance for metal dissolution, Ω cm^2
R_p	Polarisation resistance, Ω cm^2
R_s	Uncompensated solution resistance, Ω cm^2
R_t	Charge transfer resistance, Ω cm^2
S	Solubility of oxygen in the electrolyte solution, M
S_0	Solubility of oxygen in pure water, M
sce	Saturated calomel electrode
she	Standard hydrogen electrode
t_{corr}	Corrosion time, hours
W	Warburg diffusion impedance, Ω cm^2
x_g	Mole fraction of dissolved gas
Z'	In-phase component of impedance, Ω cm^2
Z''	Out-of-phase component of impedance, Ω cm^2
Z_f	Impedance, Ω cm^2
Z_W	Warburg diffusion impedance, Ω cm^2

Publications

(i) Refereed papers as joint author

"An electrochemical study of reduced ilmenite carbon paste electrodes", Y. Marinovich, S. Bailey, J. Avraamides, and S. Jayasekera, J. App. Electrochem. <u>25</u>:823 (1995).

"Pressure leaching of reduced ilmenite: electrochemical aspects", S. Jayasekera, Y. Marinovich, J. Avraamides, and S. Bailey, Hydrometallurgy <u>39</u>:183 (1995).

(ii) Conference Papers (Oral Presentations)

"The corrosion of pure iron by dissolved oxygen in aqueous ammonium chloride", J. Avraamides, S. Bailey, <u>Y. Marinovich</u>, and J. Pang, 10th Australasian Electrochemistry Conference, Goldcoast, 1997.

"An electrochemical investigation of the removal of iron from reduced ilmenite", <u>Y. Marinovich</u>, S. Bailey, J. Avraamides, and S. Jayasekera, AIMM Proc. Conf., 1996; p 237 .

"The electrochemistry of iron corrosion by oxygen from 30 to 150°C in ammonium chloride solutions", Y. Marinovich, Corrosion and Prevention 95, Perth, 1995.

"A high pressure high temperature rotating disk electrode study of iron corrosion by oxygen", <u>Y. Marinovich</u>, S. Jayasekera, S. Bailey, and J. Avraamides, 46th International Society of Electrochemistry Conference, Xiamen, 1995.

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