Hydrogen Production

1 Introduction

2 Fundamentals

2.1 Thermodynamics

The electrolysis process is an endothermic reaction, the enthalpy change is related to the Gibbs free energy, the energy required to split water by the following equation.

$$\delta G_R = \delta H_R - T\delta S_R \tag{1}$$

With increasing temperature, the energy required for decomposing water is reduced. This is the reason why high temperature electrolysis method is adopted for the electrolysis process.

2.1.1 The reversible cell voltage

The reversible cell voltage is the minimum voltage at which the electrolysis is possible, it is related to the Gibbs Free energy by:

$$E_{rev} = \frac{-\delta G_f}{nF} \tag{2}$$

Where F is Faradays constant, n is the number of electrons transferred per molecule of hydrogen produced. For this system, n=2. At standard condition, it can be shown that:

$$\delta H^0 = +298 KJmol^{-1} \quad \delta G^0 = +237 KJmol^{-1} \tag{3}$$

The reversible cell voltage at standard condition is therefore 1.228V.

2.1.2 Thermo neutral potential

The Thermoneutral voltage Etn describes the potential, at which the process in the electrolysis cell is neither endothermic nor exothermic; the electrical losses equal the heat required by the endothermic electrolysis process

and describes the total energy demand for the reaction. At standard conditions, this is 1.49V.

$$E_{tn} = \frac{-\delta H_f}{nF} \tag{4}$$

Between the thermo neutral potential and reversible cell voltage, isothermicity can not be maintained and the cell would absorb heat from the surroundings.

2.1.3 Temperature and pressure dependency

Reversible cell voltage is related to temperature and pressures by

$$E_{rev}(T,p) = E_{rev}(T) + \frac{RT}{zF} ln[\frac{p - p_v)^{1.5} p*_v}{P_v}] \tag{5}$$

Temperature effects on reversible cell voltage(the first term) can be shown to be: