Effect of Temperature on the Electrolysis of Water in Concentrated Alkali Hydroxide Solutions

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The electrochemical conversion of water to hydrogen and oxygen, electrolysis, represents a critical technology in the development of distributed hydrogen production systems. The production of hydrogen from electrolysis which is powered by renewable energy sources (*i.e.*, solar, wind, geothermal, *etc.*) furthers U.S. interests to provide a renewable, clean energy source to reduce dependence on foreign fuels, reduce pollution of the environment, and provide for increasing energy demands. Significant use of hydrogen will contribute to reduced CO_2 emissions and reduce pollution from CO, NO_x, SO_x, NMHC (non-methane hydrocarbons), and particulates. Currently, *ca.* 96% of the global hydrogen production is derived from the reforming of fossil fuels (natural gas, gasoil),[1,2] which are not renewable energy sources and contribute to carbon dioxide emissions. The need for renewable, clean energy sources is enhanced by the increasing worldwide energy consumption, which is expected to double by mid-century.[3]

Electrolysis of water to hydrogen and oxygen may be achieved in either acidic, neutral, or alkaline electrolytes. Electrolysis within an alkaline electrolyte occurs by the combination of cathodic (eq. 1) and anodic (eq. 2) half-cell reactions and results in the overall conversion of water to hydrogen and oxygen (eq. 3) as described by the following equations.

Cathode: $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ (1)

Anode: $2\ OH^- \rightarrow \frac{1}{2}\ O_2 + H_2O + 2e^-$ (2)

Net Reaction: $H_2O \rightarrow H_2 + \frac{1}{2}\ O_2$ (3)

Maximizing the electrolysis efficiency and minimizing cost are critical steps to develop cost-effective hydrogen production systems. Previous experimental and theoretical work has shown that the electrochemical potential for water dissociation to H_2 and O_2 is a strong function of temperature and pressure.[4,5] In particular, the theoretical electrochemical potential required to split water decreases substantially with increasing temperature and pressure.[5] To take advantage of the better kinetic and thermodynamic conditions that occur at higher temperatures, previous work has also been aimed at involved the development of improved membranes to allow electrolysis at elevated temperatures.[6]

In order to maximize the efficiency of water electrolysis, Lynntech has investigated the effect of temperature on electrolysis in concentrated alkali hydroxide solutions. Concentrated alkali hydroxide solutions are attractive candidates for high temperature electrolysis based on the observation that saturated aqueous solutions of sodium hydroxide do not boil at one atmosphere, as further reflected in their phase diagram.[7] Based on this unique property, concentrated alkali hydroxide solutions can allow the electrolysis of water over a wide range of temperatures and pressures.

An initial design for a high temperature electrolysis cell was developed. Current-voltage measurements were obtained as a function of temperature, and initial results using unoptimized electrodes are shown in Figure. 1. These experiments demonstrate that increasing the cell temperature considerably lowers the voltage required for electrolysis. The results also suggest that in addition to current density, cell temperature should be considered as an important factor in maximizing system efficiency. The effect of temperature on water loss and the stability of cell components must also be considered. Lynntech is currently developing components (electrodes, electrolytes, cell designs, *etc.*) to maximize cell efficiency.

Concentrated alkali hydroxide solutions may be particularly attractive candidates for developing low-cost high efficiency electrolyzers which operate at elevated temperatures (above 100 ºC). Potential sources of heat to increase the cell temperature may include solar, geothermal, nuclear, and other sources where waste heat is generated and not normally utilized. The development of low-cost, high efficiency electrolyzers may contribute to the development of improved distributed hydrogen generation systems for automobile refueling, military applications (unmanned aerial vehicles, *etc.*) and other systems.

Figure 1. Initial results of dependence of electrolysis voltage on temperature and current density; data obtained in concentrated alkali using unoptimized electrodes.

Temperature	Current density (mA/cm^2)		
(ºC)	50	100	500
25	1.95	2.05	2.42
50	1.93	2.02	2.39
100	1.64	1.72	1.94
150	1.49	1.63	1.91
175	1.53	1.64	1.86
200	1.49	1.51	1.85
250	1.31	1.37	1.65

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