

Electrochemical Investigation of Alloys For Alkaline Water Electrolyzers

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ABSTRACT

In alkaline water electrolyzers many parts are made of expensive nickel-based alloys, which in some cases may be an overly conservative option. Careful evaluation of the operating conditions and new research are required to determine to which extent nickel-based alloys may be replaced by less expensive materials in parts of the system.

Electrochemical investigations have been carried out to get a deeper understanding of corrosion and film formation occurring on typical alloys used in alkaline electrolyzers. Potentiodynamic sweeps were performed on carbon steel (UNS K03014) and austenitic stainless steel (UNS S31603) in 25 wt% KOH under O₂, N₂ and H₂ at atmospheric pressure from room temperature up to 80 °C. The gases represent the anode side, start-up/shut-in and the cathode side, respectively. Differences between the two materials and their response at the different conditions are discussed.

Key words: alkaline, corrosion, carbon steel, stainless, films

INTRODUCTION

The global renewable energy market is fast growing with a focus on solar and wind. These are intermittent energy sources that are subject to both seasonal and hourly variations, generating significant amounts of excess energy (several TWh/year worldwide) that will have to be stored before utilization. Power-to-Gas technologies, such as water electrolysis, are expected to play a major role in future energy storage systems. Hydrogen production by water electrolysis is highly appropriate for storage of large amounts of intermittent renewable energy.¹

Although polymer electrolyte membrane (PEM) electrolyzers have the best performance for water electrolysis, the complexity of the system with its high pressure operation and the high cost – mainly due to the use of noble metal catalysts – have prevented commercialization thus far.^{2,3}

An established alternative is alkaline water electrolysis. These operate at lower current densities, but are less expensive and thereby suitable for large-scale hydrogen production.⁴ Current R&D typically aim to increase efficiency and decrease operational expenses (OPEX). One strategy is to decrease the cell

voltage, which can potentially be achieved by zero-gap systems,⁴ or increasing the current density and operating pressure.³

Electricity cost and other OPEX will vary with time and their contribution to the total life cycle cost is uncertain at the time of purchase. Reduced capital expenses (CAPEX) are therefore expected to make the use of alkaline electrolyzers more economically attractive. Materials for the various parts of the electrolyzer (cell stacks, separators, electrolyte loops etc.) are a significant part of the CAPEX, especially for pressurized electrolyzers. A strategy towards reducing the total cost of an electrolyzer system is therefore to cut down on the use of the most expensive alloys (nickel-based) and explore the possibility of using cheaper options such as stainless or carbon steels with or without coating/cladding.¹

Several publications investigating electrochemical properties of transition metals and transition metal oxides in alkaline solution are available. Most of the literature is related to electrode materials and catalysts⁵ and not typical materials for balance of plant (BoP) per se. In terms of the materials themselves, there is significant overlap between electrodes and BoP. For example, iron, nickel and chromium alloys and oxides are interesting for both applications and knowledge is indeed transferrable.

Electrode studies, however, are usually focused on either oxygen or hydrogen evolution, meaning that the potential region studied is usually at either the anodic or the cathodic⁶ end, while for BoP materials the most interesting potential region is the one in between. Also, many laboratory studies in alkaline solution are restricted to 1 M KOH (or 1 M NaOH) at 25 °C while the industrial process of alkaline water electrolysis is typically carried out in 25 wt% KOH at 80 °C.

This work aims to carry out electrochemical characterization of carbon steel (UNS K03014) and austenitic stainless steel (UNS S31603) at industrial conditions in order to provide information relevant for design and material selection. The conditions investigated, i.e. O₂, N₂ and H₂ at atmospheric pressure from room temperature up to 80 °C were chosen to represent the anode side, start-up/shutdown, and the cathode side.

EXPERIMENTAL PROCEDURE

Electrochemistry

Electrochemical measurements were carried out using a 3-electrode setup using carbon steel or stainless-steel cylinders with 1 cm height and 1 cm diameter as working electrodes, a platinum coil as counter electrode and a Hg/HgO (in 20 wt% KOH) reference electrode. The total pressure was 1 atm for all tests and the electrolyte was 25 wt% KOH in distilled water. Experiments for carbon steel in N₂, air and O₂ at 25 and 40 °C were carried out in a glass cell, while the remaining experiments were carried out in a 2 L UNS N10276 autoclave with a customized polymer lid. All experiments were carried out with continuous purging of the relevant gas, keeping the gas flow rate constant at 50-100 mL/min by means of a mass flow controller. Magnetic stirring was enabled during the experiments.

Potentiodynamic sweeps were carried out by first recording the cathodic scan from open circuit voltage (OCV) down to -1200 mV vs. Hg/HgO with a sweep rate of 0.2 mV/s. After allowing the potential to relax for at least one hour the anodic scan was recorded from OCV to +750 mV vs Hg/HgO, still with a sweep rate of 0.2 mV/s. Experiments were recorded in a cyclic manner, meaning that the potential was scanned from the start potential to the end potential and back to start. When shown on a linear scale both forward and reverse scans are included, while semilogarithmic Tafel plots are shown selecting the first part only.

For experiments using stainless steel working electrodes, and for carbon steel in H₂, the same electrode was used for three temperatures with the same purge gas, starting with the lower temperature. For the carbon steel tests, the same electrode was used for N₂ and O₂ at 25 and 40 °C. The use of a glass cell allowed visual observation of the electrode surface throughout, and no visible change in the electrode

surface could be identified at either temperature following tests in N₂ (nor in some intermediate tests in air which are not included in this work).

Experimental conditions are summarized in Table 1 and Table 2, where the ID tags are constructed to represent material-gas-temperature. For example, C-O-25 means carbon steel in O₂ at 25 °C.

Table 1: Summary of experimental conditions for carbon steel working electrodes

Exp. ID	Electrode UNS	Temp. (°C)	Purge gas	p_i (bar)	KOH (wt%)
C-N-25	K03014	25	N ₂	-	25
C-N-40	K03014	40	N ₂	-	25
C-N-80	K03014	80	N ₂	-	25
C-O-25	K03014	25	O ₂	0.99	25
C-O-40	K03014	40	O ₂	0.96	25
C-O-80	K03014	80	O ₂	0.66	25
C-H-25	K03014	25	H ₂	0.99	25
C-H-40	K03014	40	H ₂	0.96	25
C-H-80	K03014	80	H ₂	0.66	25

Table 2: Summary of experimental conditions for stainless steel working electrodes

Exp. ID	Electrode UNS	Temp. (°C)	Purge gas	p_i (bar)	KOH (wt%)
S-N-25	S31603	25	N ₂	-	25
S-N-40	S31603	40	N ₂	-	25
S-N-80	S31603	80	N ₂	-	25
S-O-25	S31603	25	O ₂	0.99	25
S-O-40	S31603	40	O ₂	0.96	25
S-O-80	S31603	80	O ₂	0.66	25
S-H-25	S31603	25	H ₂	0.99	25
S-H-40	S31603	40	H ₂	0.96	25
S-H-80	S31603	80	H ₂	0.66	25

RESULTS

Current-voltage responses shown on the linear scale are not corrected for the uncompensated resistance (IR-drop) or for liquid junction potential associated with the reference electrode. Values for uncompensated resistance, as estimated from the minimum real value of the impedance, ranged from 0.8 to 1.6 $\Omega \cdot \text{cm}^2$. With current limits in the figures of $\pm 4 \text{ mA} \cdot \text{cm}^{-2}$, this would introduce a voltage error of up to 6.4 mV at the maximum current displayed. The maximum liquid junction potential between 20 wt% KOH in the reference chamber and 25 wt% in the autoclave can, by use of the Henderson equation,⁷ be estimated as 2.6 mV (note assumptions of infinite dilution theory implicit in this calculation). Since the reference electrode was placed inside the autoclave, diffusion through the porous frit is expected to decrease concentration gradients and hence the liquid junction potential with time.

Electrochemistry of carbon steel

Cyclic potentiodynamic sweeps of carbon steel in H₂ atmosphere are shown in Figure 1 for all temperatures (25, 40 and 80 °C). Rapidly increasing currents at the cathodic and anodic ends represent H₂ and O₂ evolution, respectively. The cathodic sweep at 25 °C has an anodic peak around -0.84 V in

the reverse scan, i.e. in the anodic scan direction after first scanning down to -1.2 V. At 40 °C the same peak is the dominating feature, but now two shoulders at -0.72 and -0.67 V are also visible, cf. the inset in Figure 1. In the 80 °C experiment OCV was around -0.97 mV, so the cathodic scan captured hydrogen evolution only. Here the anodic peaks described above are visible in the forward part of the anodic scan. The current (charge) associated with the peaks increases with increasing temperature.

Carbon steel in N₂ atmosphere, shown in Figure 2, display qualitatively the same features as in H₂. The anodic peak at 40 °C is larger than in H₂ atmosphere and somewhat shifted to lower potentials (max current at -0.85 V). For the experiment at 80 °C a significant shift in potential (around 0.35 V) is observed for the anodic peak. Note, however a corresponding shift in the H₂ current and the absence of an O₂ current. This, and the observation of noisy currents, leads to the conclusion that the apparent potential shift is most likely due to issues with the reference electrode.

Figure 3 shows cyclic potentiodynamic sweeps of carbon steel in O₂ atmosphere. OCV was now shifted positively to around -0.2 V and consequently the anodic peaks (cf. the peak with a maximum current at -0.86 mV at 80°C) are now apparent in the cathodic sweeps, after reversal, for all temperatures. Also visible are now two cathodic waves. The inset zoom of the 40 °C curve shows them more clearly. At 80 °C only the more positive of the two is observable, while the more negative one is hidden by the H₂ evolution current. In the inset also an oxidation plateau starting around 0 V can be seen in the anodic scans.

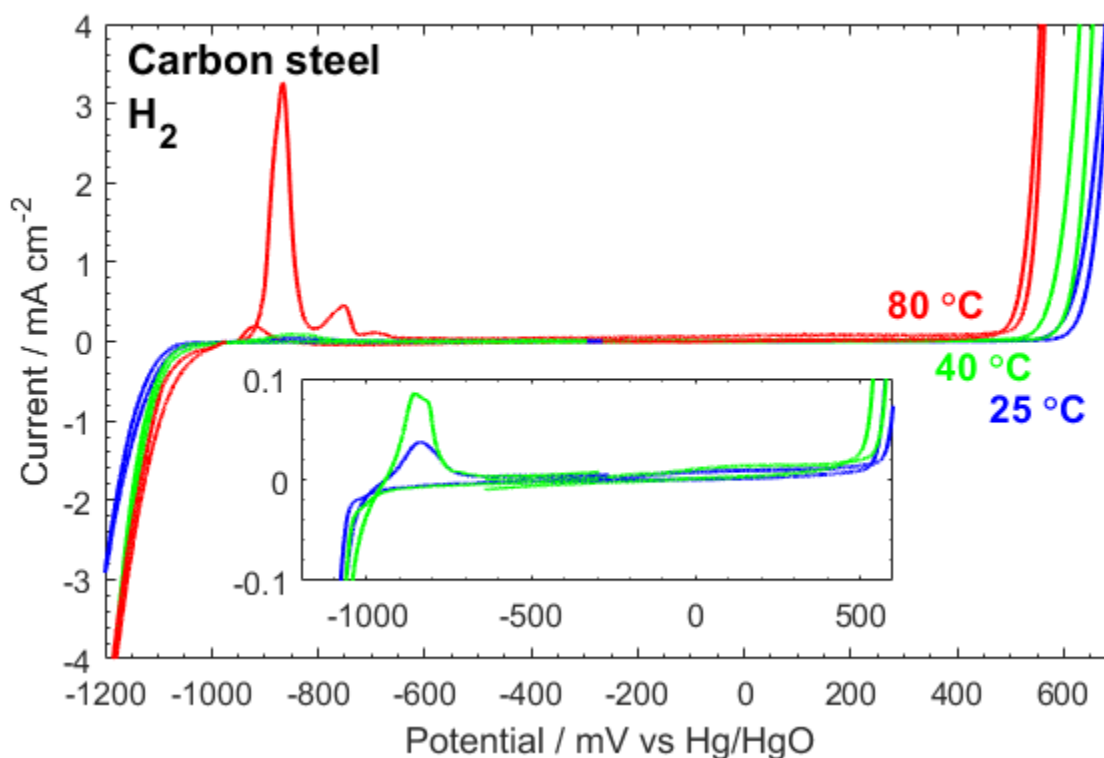


Figure 1: Cyclic potentiodynamic scans of a carbon steel electrode in H₂ atmosphere at 25, 40 and 80 °C. The inset shows a zoom of curves from the 25 and 40 °C experiments.