

## Effects of Chloride Ions on Transient Current after Potential Shift to Pt Oxide Formation Region in 553K Hydrogenated LiOH-H<sub>3</sub>BO<sub>3</sub> Solutions Containing Chloride Ions

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**\*Keywords :** chloride concentration, transient current, hydrogen oxidation

### 1. Introduction

We've provided insights [1] into the behavior of H<sub>2</sub> oxidation at Pt electrodes under conditions of high temperature. In our experiment at 473 K, we noticed an interesting range of potential where the current reached a minimum value, positioned between the areas of dissolved H<sub>2</sub> oxidation and the water oxidation potential at the Pt electrode. This occurrence was explained by the development of a layer of Pt oxide [1]. We also explored the potential for monitoring Cl<sup>-</sup> concentrations through an examination of the transient behavior of H<sub>2</sub> oxidation [2]. However, previous studies only briefly mentioned the existence of this unique phenomenon and the feasibility of monitoring Cl<sup>-</sup> concentrations. They lacked a comprehensive analysis of the behavior of H<sub>2</sub> oxidation at high temperatures, the formation of the Pt oxide layer, and the impact of Cl<sup>-</sup> ions. In reality, both Cl<sup>-</sup> ions and other halide ions like bromide and iodide can impede the formation of a Pt oxide layer. Nonetheless, our focus was on Cl<sup>-</sup> ions, which could be present in a nuclear reactor coolant system.

In this study, we compared the concentration of Cl<sup>-</sup> ions with the current generated by the oxidation of dissolved H<sub>2</sub>, examining both steady-state and transient conditions. We reinterpreted the relationship between the concentration of Cl<sup>-</sup> ions and the transient current by considering the formation of the Pt oxide layer. This research aids in understanding the effects of impurities such as Cl<sup>-</sup> ions on the oxidation behavior of dissolved H<sub>2</sub> and the rate at which the Pt oxide layer forms at high temperatures.

### 2. Methods and Results

#### 2.1 Loop and Electrochemical System

A loop arrangement was employed for studying the behavior of dissolved H<sub>2</sub> on a Pt surface at high temperatures. The loop setup primarily comprised a high-temperature electrochemical cell, a potentiostat system, and a rod-shaped electric heater, illustrated in Fig. 1. The flow rate and pressure of the solution circulating within the loop were adjusted to 0.5 cm<sup>3</sup>·min<sup>-1</sup> and 15 MPa using a metering pump (Teikoku) and a back pressure regulator (Tescom). The solution

circulating in the loop was created by combining reagent-grade LiOH and H<sub>3</sub>BO<sub>3</sub>, and its temperature was regulated within the range of 298 – 553 K by a rod-type electric heater. The solution's temperature was specifically controlled between the electric heater and the water cooling jacket, while other components were maintained at room temperature.

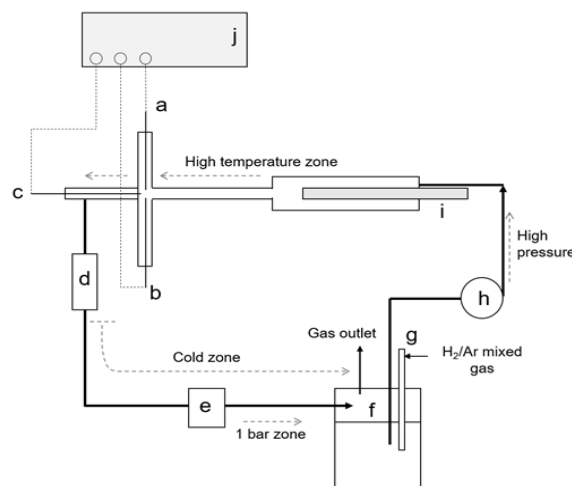


Fig. 1. Scheme of high temperature electrochemical measurement loop system: a) Pt electrode; b) Ag/AgCl reference electrode; c) Pt counter electrode; d) water cooling jacket; e) back pressure regulator; f) solution reservoir; g) H<sub>2</sub> gas bubbler; h) injection pump; i) electric heater; j) potentiostat system [3]

In the electrochemical setup, a Pt rod and a Pt wire with a 1 mm diameter were utilized as the working and counter electrodes, correspondingly. The exposed surface areas of these electrodes were 0.1 cm<sup>2</sup> and approximately 2 cm<sup>2</sup>, respectively. Furthermore, a 0.1 M KCl Ag/AgCl electrode was employed as an external reference electrode. Potentiodynamic polarization and potential transient techniques were employed to analyze the electrochemical behavior of the dissolved H<sub>2</sub> and to identify chloride ions within the hydrogenated solution. Electrochemical measurements were carried out using a potentiostat system (Bio-Logic SAS) and controlled through dedicated application software (EC-Lab). All electrochemical potentials used in this study reflect the actual applied potentials based on the external reference

electrode, without adjustments for the thermal liquid junction potential.

## 2.2 Polarization Behavior of $H_2$ Oxidation According to $Cl^-$ Concentration

Before the transient experiment, potentiodynamic polarization curves of the Pt electrode were acquired in 553K hydrogenated  $LiOH-H_3BO_3$  solutions containing varying  $Cl^-$  concentrations. The applied potential was incrementally scanned in the direction of the oxidation potential, ranging from  $-0.8 V_{Ag/AgCl}$  to  $1.2 V_{Ag/AgCl}$ , at a scan rate of  $1 mV min^{-1}$ . As illustrated in Fig. 2a, the obtained polarization curves portrayed the Pt electrode's behavior within the high-temperature hydrogenated aqueous solutions. The influence of the  $Cl^-$  concentration on the polarization curves was scarcely noticeable.

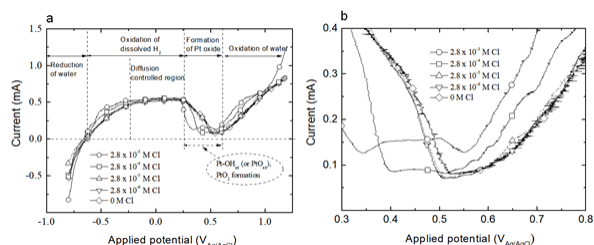


Fig. 2. **a** Potentiodynamic polarization curves of the Pt electrode in a 32 mM  $H_3BO_3$  solution containing 0.43 mM  $LiOH$  hydrogenated with  $1.6 \times 10^{-4} M H_2$  and with chloride ion at a solution temperature of 553 K:  $2.8 \times 10^{-3} M$  (O),  $2.8 \times 10^{-4} M$  (□),  $2.8 \times 10^{-5} M$  (Δ),  $2.8 \times 10^{-6} M$  (▽) and  $0 M$   $Cl^-$  ion (◇); scan rate,  $1 mV s^{-1}$ ; exposed electrode area,  $0.1 cm^2$ . **b** An enlarged view of the current in the valley potential region of Fig. 2a.[3]

## 2.3 Electric charges of $H_2$ Oxidation According to $Cl^-$ Concentration

In Table 1, a comparison was conducted regarding the initial maximum oxidation current subsequent to the application of the valley potential, as well as the quantities of electric charges following intervals of 0.01 s, 0.1 s, and 1.0 s, based on varying  $Cl^-$  concentrations. The shorter the cumulative time (in the sequence of initial maximum oxidation current, quantities of electric charges for 0.01 s, 0.1 s, and 1.0 s), the more responsive the transient current (or charge) proves to be in relation to the  $Cl^-$  concentration. This signifies that  $Cl^-$  ions exhibit a more noticeable influence in the initial stages of oxide layer growth—specifically, during the formation of a thin Pt oxide layer—than during the process of developing a thicker oxide layer.

While our experimental outcomes may not allow for a precise quantification of the impact of  $Cl^-$  concentration on the growth rate of the Pt oxide layer and the correlation between Pt oxide layer expansion and  $H_2$  oxidation current, our current transient outcomes

unambiguously indicate the potential to detect  $Cl^-$  concentrations in high-temperature hydrogenated solutions, reaching levels of at least  $2.8 \times 10^{-5} M$ .

Table I: Initial current ( $t = 0 s$ ) and quantities of electric charges according to  $Cl^-$  ion concentration [3]

$Cl^-$ conc. ( $\mu M$ )	Current (mA) at $t = 0$	Quantity of electric charge (mC)		
		0 - 0.01 s	0 - 0.1 s	0 - 1.0 s
0	1.57	0.0167	0.1303	0.9166
2.8	1.60	0.0173	0.1341	0.9328
28	1.69	0.0179	0.1391	0.9594
280	2.740	0.0266	0.1765	1.1055
2,800	12.844	0.0884	0.4699	1.5538

## 3. Conclusions

The  $H_2$  oxidation current at the Pt electrode exhibited an increase alongside the rise in dissolved  $H_2$  concentration within the high-temperature  $LiOH-H_3BO_3$  solution. The ability to detect  $Cl^-$  concentrations below  $2.8 \times 10^{-3} M$  using polarization curves under steady-state conditions within hydrogenated high-temperature solutions proved challenging. However, transient currents of  $H_2$  oxidation measured during the Pt oxide layer's growth were capable of detecting  $Cl^-$  concentrations as low as  $2.8 \times 10^{-5} M$ . This is attributed to the impact that even an extremely low concentration of  $Cl^-$  ions can exert on the Pt oxide layer's growth rate.

## Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) Grant funded by the Korean government (MSIT) (NRF-2017M2A8A4015281, 2021M2E3A3040092, RS-2022-00144202, RS-2023-00261146).

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