



# Redox potential measurements in the $\text{H}_2\text{SO}_4\text{-FeSO}_4\text{-Fe}_2(\text{SO}_4)_3\text{-H}_2\text{O}$ system at high temperature using an Ir electrode



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## ABSTRACT

An Ir electrode was evaluated as a suitable alternative to Pt for redox potential measurements at high temperature and high pressure. Measurements were performed using a flow-through electrochemical cell (FTEC) with a Ag/AgCl in 0.1 M LiCl flow-through external pressure-balanced reference electrode (FTEPBRE), at a flow rate of 0.5 mL/min, 35 atm (500 psia) and up to 200 °C. The potential was measured for the  $\text{H}_2\text{SO}_4\text{-FeSO}_4\text{-Fe}_2(\text{SO}_4)_3\text{-H}_2\text{O}$  system for concentrations of 1 M  $\text{H}_2\text{SO}_4$ ,  $10^{-2}$  M Fe(III), and  $10^{-4}\text{--}10^{-2}$  M Fe(II) (ratios of [Fe(II)]/[Fe(III)] equal to 0.01, 0.1, and 1 respectively). The potentials measured with the Ir electrode were similar to those obtained using a Pt electrode, with a maximum difference of 8 mV over the range of studied solutions and temperatures. The change in potential measured with the Ir electrode behaved according to the Nernst equation upon changes in the test solution, and were consistent with the corresponding estimated potential variation predicted by the Aqueous (OLI-AQ) model from the OLI<sup>®</sup> aqueous chemistry simulation software ([www.olisystems.com](http://www.olisystems.com)).

## 1. Introduction

The redox potential is one of the most significant and widely used process variables for characterization and control in aqueous reacting systems because it is fairly easy to measure and because it provides insight into redox reactions. As a consequence, monitoring and control of the redox potential is important in industrial processes, especially those processes operating at high temperatures, because it provides an opportunity for in situ measurement without the biases introduced during sampling systems at high temperature and pressure, which then have to be cooled and measured under atmospheric pressure. In the metals industry, implementation of redox sensors in industrial scale autoclave reactors has been delayed due to the highly corrosive nature and the existence of mineral particles at high percent solids. Examples of hydrometallurgical processes that could benefit from the development of a robust redox sensor in the mining and metals industry are pressure leaching of base metals such as copper, zinc, and nickel, as well as pressure oxidation of refractory ores and concentrates to recover gold [1–3].

Potentiometric measurements at high temperature with the objective to measure pH by means of Pt/H<sup>+</sup>/H<sub>2</sub> working electrodes have been reported in the literature mainly for dilute solutions up to su-

percritical temperatures [4–12]. Hydrometallurgical processes at high temperature deal with multicomponent concentrated solutions and oxidizing environments, including systems with chlorides that allow for Pt dissolution and formation of stable chloro-complexes. This would decrease the lifetime of the Pt electrode and introduce errors by providing a mixed potential reading, which would include an additional potential contribution corresponding to the dissolution of the platinum electrode into the solution being characterized. Ir is almost as noble as Pt [13], however, in the presence of chloride ions, the potential for the reduction of chloro-complexes to the metal is higher for Ir than for Pt, i.e., 860 mV vs. 758 mV, respectively, at room temperature [13], making Ir more inert to the presence of chloride ions. Also, Pt-Ir alloys have been tested for the electrochemical production of chlorine since such an electrode is not subject to corrosion phenomena in acid solutions containing Cl<sup>-</sup> and Cl<sub>2</sub> [14,15]. Ir/IrOx sensors have also been proven to function as reliable pH sensors [16–19] at temperatures up to 175 °C [20], although with only partial success up to 250 °C [21].

The objective of this paper is to evaluate the suitability of an Ir electrode as a reliable working electrode for redox potential measurements at high temperatures and high pressures, and its prospects for use in industrial processes that operate over 150 °C.

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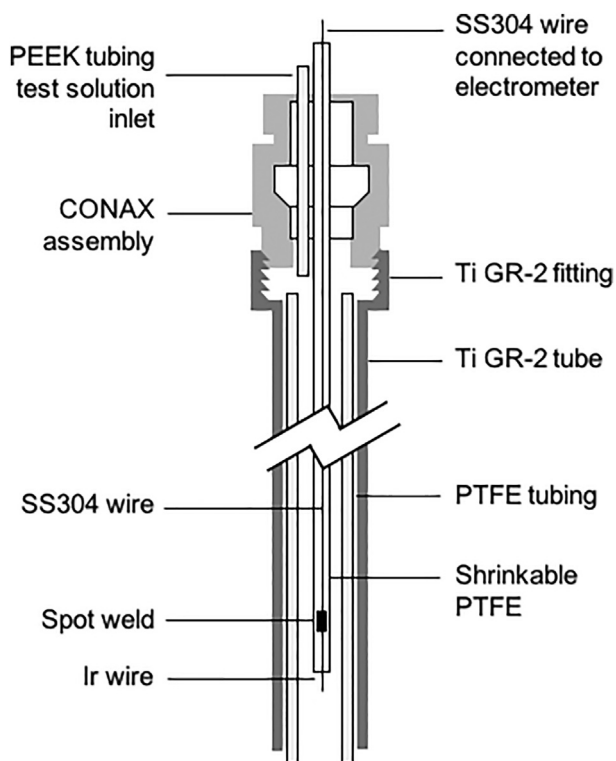


Fig. 1. Schematic diagram of the Ir electrode.

## 2. Materials and methods

### 2.1. Electrode preparation

The reference electrode was a Ag/AgCl flow-through external pressure-balanced reference electrode (FTEPBRE) prepared according to procedures well-established in the literature [22]. The working electrode was an Ir wire, 0.5 mm in diameter, 13 cm in length (Alfa Aesar, 99.8% pure), spot welded to a SS304 wire 0.5 mm in diameter (Alfa Aesar). Approximately 5 mm of the tip of the electrode was in contact with the test solution at high temperature. The rest of the electrode was covered in heat shrinkable PTFE to provide insulation from the solution. The Ir electrode was pressure sealed using a CONAX assembly. A schematic diagram of the Ir electrode is shown in Fig. 1.

### 2.2. Apparatus

A schematic diagram of the flow-through electrochemical cell (FTEC) experimental setup is shown in Fig. 2.

Lvov et al. [4,5,22,23] successfully used the FTEC design concept for pH measurements in solutions of dilute acid at high temperature. The same methodology was subsequently adopted by the Arai group [6–12]. A modified setup was also used by Jankovic et al. [24,25] to measure pH in concentrated industrial solutions at high temperature. In the present work further modifications were made as described below.

The cell consisted of two tubes. The first tube was made of titanium GR-2, which housed the Ir electrode and had an inner PTFE tube to isolate the Ir electrode from the titanium walls. The second tube was made of polyether-ether ketone (PEEK) and was used to introduce the

reference solution (Fig. 2). In order to facilitate mixing of the reference and test solutions, a commercially available titanium GR-2 T-shaped connector joined the two tubes. The resulting mixture was directed outside of the cell. The flow-through electrodes were sealed and isolated from their respective tubes using CONAX assemblies.

The portion of the cell that housed the tip of the Ir electrode was heated using a heating cord wrapped around the titanium tube. The heated area was surrounded with a ceramic fiber blanket to provide thermal insulation and improve temperature stability to  $\pm 0.5$  °C. Temperature was measured using a J-type thermocouple and controlled using a CN 77000 series temperature controller (OMEGA). The tip of the thermocouple was located immediately next to the tip of the Ir electrode and it was covered with heat shrinkable PTFE to prevent corrosion and direct contact with the Ir electrode. Pressure was monitored using a pressure gauge and a pressure transducer, and controlled using a pressure relief valve. Reference and test solutions were sparged with  $N_2$  before and throughout the experiment to remove dissolved  $O_2$  and avoid possible oxidation of  $Fe^{2+}$ . The potential difference between electrodes was measured using an electrometer with an input impedance of  $10^{14}$   $\Omega$  (Keithley 617).

### 2.3. Measurement procedure

Prior to measurement in the FTEC, the Ir electrode was cleaned by polishing using a polycrystalline diamond suspension 15  $\mu m$  (MetaDi® Supreme), then sonicated in acetone, and finally sonicated in 1 M  $H_2SO_4$ . The Ir electrode was then tested at room temperature against a commercial Ag/AgCl reference electrode (Accumet glass body, single junction, filling solution 4 M KCl + saturated AgCl, from Fisher Scientific) and against a Ag/AgCl electrode immersed in 0.1 m LiCl, prepared in the laboratory. The potential was measured in a beaker provided with agitation. The compositions of the test solutions are given in Table 1. The potential was first measured using a commercial platinum half-cell electrode (Fisher Scientific) and compared with the results obtained with the Ir working electrode. The potential difference between the electrodes was measured using the Keithley 617 electrometer.

For the potential measurements using the FTEC, reference and test solutions were pumped through the corresponding electrodes at a constant rate, 0.5 mL/min, and constant pressure, 35 atm (500 psi) using two Chem Mate Digital high-accuracy HPLC pumps (Rose Scientific) with non-metallic internals. The potential was measured until reaching a stable value of  $\pm 1$  mV. The temperature was then increased to a new set point and the potential was measured again for 20 min. This procedure was followed at 23 (room temperature), 40, 80, 120, 160, and 200 °C, respectively. The measured potential followed an instant response to changes in temperature. The stabilization of the measured potential was related to variations in the temperature as it reached the set point rather than the instability of the Ir electrode. Temperature and potential stabilized within 5 min. After measuring the potential at 200 °C the system was cooled down and the potential was again measured at room temperature and compared with the value obtained at the beginning of the measurement. If the room temperature potential at the beginning and end of the experiment differed by more than 5 mV, the results were discarded and the working electrode was cleaned to prepare for new measurements. A maximum temperature of 200 °C was selected in order to preserve the physical and chemical integrity of the materials, particularly PTFE.

The test solutions are described in Table 1. The composition of the test solutions was selected in order to avoid precipitation of  $Fe_2O_3$  (hematite) at high temperature. The reference solution was 0.1 m LiCl

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