

# Application of Soret phenomenon to electrochemical sensor response improvement

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## Introduction

The gradient of concentration in Nernst layer is the driving force which assures the mass transport to the electrode. The diffusion is generally slow. It is desired to improve the electrode response and sensitivity which means to make the mass transport more intensive. There are two possibilities:

1. Decrease due to hydrodynamic forces the effective Nernst layer thickness which increases the gradient of concentration as driving force responsible for the mass transport through Nernst layer.
2. Add another driving force to induce the additional mass flow through Nernst layer to the electrode surface.

The poster presents the use of temperature gradient as driving force for thermodiffusion to make the mass transport to the electrode more intensive. The sensors with electrodes system - working electrode, reference electrode and auxiliary electrode and heating system consisting of two resistors and temperature sensing element were integrated on the ceramic base. The advantage of ceramics lies in the fact that the thermal conductivity is very high and in case of BeO ceramics comparable with metals. It enables precise control of working electrode temperature and applying the temperature gradient exclusively to the Nernst layer.

Material	Specific heat conductivity W/m.K
water at 25 °C	0,606
Al <sub>2</sub> O <sub>3</sub> ceramics	35
BeO ceramics	180
Ag	420



Electrochemical sensor with integrated resistors

## Theoretical principles

The response of electrochemical reaction is controlled by three main phenomena :

1. Electrode reaction rate
2. Diffusion in Nernst layer
3. Mass transport from bulk of sample to the Nernst layer boundary

The last point is generally underestimated. The simple solution which solves all three points for screen printed electrodes is presented.

The initial conditions are: The electrolysis cell is sufficiently large that the bulk concentrations of Ox and Red are unchanged from the initial values even after electrolysis has been running for a certain time.

In the most simple case it is possible to consider  $D_{Ox} = D_{Red} = D$  and  $\sigma_{Ox} = \sigma_{Red} = \sigma$ .

If temperature gradient is present, the current approaches steady state value given by equation:

$$i = n.F.A.C_0 \frac{D}{1 + \theta(T_1)} \cdot s_T \cdot \alpha \cdot (T_1 - T_2)$$

Where  $T_1$  – temperature of the electrode surface,  $T_2$  – temperature of bulk solution,  $D$  – diffusion coefficient,  $C_0$  – initial concentration,  $s_T$  – Soret coefficient,  $\alpha$  – proportionality constant,  $\theta$  – exponential term of Nernst equation.

## Measurement set-up and Sensor

Measurement was carried out in glassy vessel with conic stirrer which was stirring except CV scans were being made. Electrochemical sensor (BVT Technologies) with incorporated heating circuit was used. Glassy vessel was placed in a small thermostat TK-1 (KEVA). Whole measuring electrochemical cell can be seen in the Fig.2.

Section of sensor with heating circuit in a contact with measuring solution is depicted in the Fig. 1.

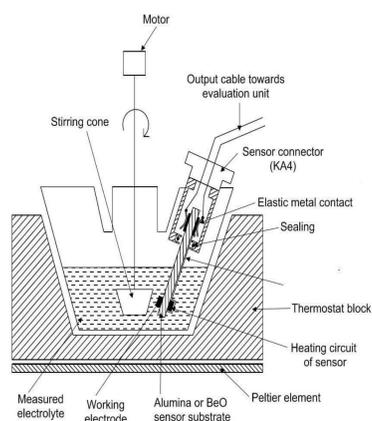


Fig. 2: Schema of the Soret system

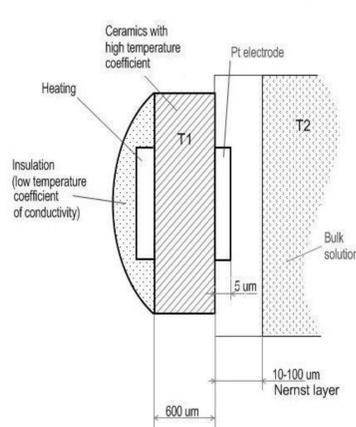


Fig. 1: Schematics of temperature gradient application on planar electrode realised on ceramics and immersed in analyzed solution

## Results

Cyclic voltammetry in the environment of Fe(II)/Fe(III) (ferro and ferricyanide) was done. Scans with and without of temperature gradient were performed. Cyclic voltammograms are shifted to higher current values with growing temperature difference because the liquid temperature was kept constant and the electrodes temperature was increased. Therefore the exponential term  $\theta(T_1)$  was changing and the curve had to move.

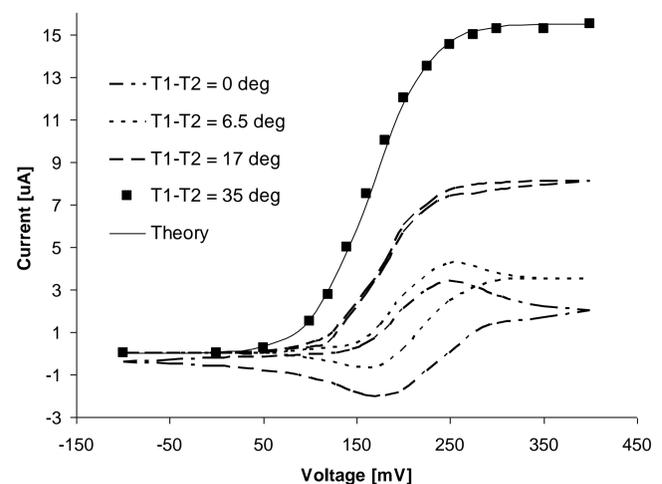


Fig.5. The change of cyclic voltammetry with applying of different thermal gradients in case of full redox couple ferro and ferri cyanide. The ■ points are experimental points for temperature difference 35 °C and the full line is the theoretical run.

## Conclusion

The time dependence of sensor response disappears when applying Soret phenomenon. The sensor current stabilizes to constant value. Efficient signal filtration is thus enabled and the sensitivity of method increases.

Also the complicated shape of cyclic voltammogram is replaced by simple exponential curve.

Cotrell-Soret equation describing the steady-state response with applied temperature difference is then:

$$i = -n.F.A.C_0.D.s_T.\alpha.(T_1 - T_2) \frac{1}{1 + e^{\frac{nF(E - E^0)}{RT_1}}}$$

Measurement of temperature dependency of activation energies is possible as we can set exact temperature of working electrode.

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