

High Resistance Compensation Method for Surface Potential Measurement*

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Abstract. The High Resistance Compensation Method (HRCM) was developed to measure the electrode potentials of high resistance electrodes. It is essentially similar to the classical Poggendorff compensation method, but instead of an ampere-meter, the pH-meter was introduced as an indicator of complete compensation. The method was applied to measurements of the electrode potentials of a single crystal rutile (TiO₂) electrode. Electrode potentials were converted to surface potentials, and the dependency of the surface potential on pH in aqueous medium was determined.

Keywords: single crystal electrode, high resistance compensation, surface potential, rutile, Poggendorff

INTRODUCTION

Electrostatic potential at the inner plane of the Helmholtz interfacial layer (0-plane), *i.e.*, surface potential Ψ_0 , is one of the important variables affecting the interfacial equilibrium of metal oxide aqueous systems. Several attempts have been made to measure the inner surface potential at the solid/liquid interface. First, the electrode potentials of metallic surfaces covered by metal oxides were measured and converted to surface potentials.¹⁻³ The main problem with metal/metal oxide electrodes is the porosity of the oxide layer allowing direct contact of the aqueous solution with the metal. In the case of porosity, the measured potential is due to the redox equilibrium at the metal/aqueous electrolyte solution interface determined by concentrations of interacting ions that depend on the solubility of the metal oxide. In fact, these electrodes behave as "electrodes of the second kind". Later on, measurements of the surface potential were performed by Ion Sensitive Field Effect Transistors (ISFET).⁴⁻⁷ A few years ago, the problem of porosity was originally solved by constructing an ice electrode.⁸ A compact ice layer was formed on the platinum and the measured potential was a result of interfacial reactions. This approach was followed by construction of single crystal electrodes (SCrE) of different

oxides, but also of iron sulphide and silver chloride.⁹⁻¹⁴ To measure surface potential at the equilibrium condition (equal ionic adsorption and desorption rates), no current should pass through the interface. The Poggendorff compensation method satisfies the requirements, but it cannot be applied due to the high resistivity of metal oxides. An approximation is the use of high resistance voltmeters (pH-meter), but still one cannot be sure that the measured response corresponds to the equilibrium condition. In this article, the development and implementation of the High Resistance Compensation Method (HRCM) is described, which is essentially the Poggendorff compensation method, but refined so that potentials of high resistance electrodes could be measured.

High Resistance Compensation Method

The High Resistance Compensation Method (HRCM) is based on compensation of the electromotivity¹⁵ (electromotive force) of the galvanic cell by counter voltage. The condition of compensation is the state in which the magnitudes of the electromotivity of the measured cell and the applied counter voltage are exactly equal. This condition is not detected by a high sensitivity ampere-meter, like in the case of the classical Poggendorff com-

* Dedicated to Professor Zvonimir Maksić on the occasion of his 70th birthday.

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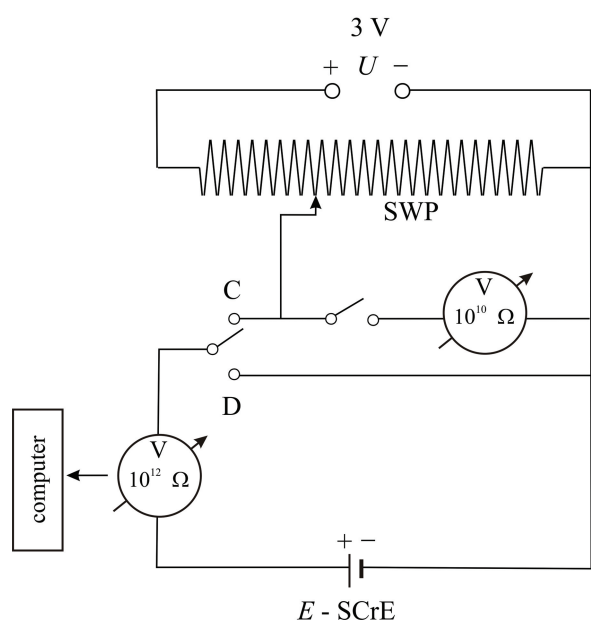


Figure 1. High resistance compensation method (HRCM) for measurements of electrode potential of the single crystal electrode (SCrE) of high resistance. The source of constant voltage of 3 V (U), slide wire potentiometer SWP, cell (E) with SCrE and reference electrode, two millivoltmeters: high resistance millivoltmeter, *i.e.*, pH-meter (V , $10^{12} \Omega$) and medium resistance millivoltmeter (V , $10^{10} \Omega$). Position D: direct measurement of electromotivity by the high resistance millivoltmeter, *i.e.*, pH-meter (V , $10^{12} \Omega$). Position C: HRCM mode.

compensation method, but by a high resistance millivoltmeter, *i.e.*, pH-meter. The setup is demonstrated in Figure 1.

The procedure is simple. In the first step (D-mode), one measures the electromotivity directly by a high resistance millivoltmeter (pH-meter, $10^{12} \Omega$). This reading is not necessarily the equilibrium value, especially if the internal resistance of the cell is not at least 100 times lower than the internal resistance of the pH-meter. In the second step (still D-mode), one adjusts the slide wire potentiometer so that the reading of the medium resistance millivoltmeter ($10^{10} \Omega$) becomes approximately equal to the value previously obtained by the high resistance millivoltmeter (pH-meter, $10^{12} \Omega$). In the third step, one switches to the HRCM-mode (C-mode) and adjusts the slide wire potentiometer so that the reading of the high resistance millivoltmeter (pH-meter, $10^{12} \Omega$) becomes zero millivolts. The electromotivity of the cell is then equal to the countervoltage as determined by the medium resistance millivoltmeter ($10^{10} \Omega$). If the reading of the high resistance millivoltmeter (pH-meter, $10^{12} \Omega$) deviates from zero millivolts, one should take this into account and add this value to the reading of the medium resistance millivoltmeter ($10^{10} \Omega$). The device is connected to a computer so that

one may observe the change in electromotivity and its constancy over a time period, as well as data scattering.

The HRCM will be analyzed and compared with conventional methods on the example of a high resistance galvanic cell of electromotivity (electromotive force) of 200 mV and the internal resistance of $10^{11} \Omega$. Misbalance of the Poggendorff bridge of 1 mV will result in electrical current of 9×10^{-16} A, which is too low to be detected. If one measures electromotivity with a pH-meter of internal resistance of $10^{12} \Omega$, the reading on the pH-meter will be 182 mV, *i.e.*, 18 mV lower than the electromotivity. The reduction would be even higher for higher internal resistance of the galvanic cell. In the case of HRCM for misbalance of the bridge of 1 mV, the current will be 9.1×10^{-19} A, which will cause a reduction in electromotivity of 0.09 mV. Since the sensitivity of the pH meter is significantly better than 1 mV, the error in evaluated electromotivity becomes negligible. The HRCM will be demonstrated for the case of a single crystal rutile electrode.

EXPERIMENTAL

Materials. All solutions were prepared using redistilled and decarbonated water: KNO_3 (*p.a.*, Kemika), HNO_3 (0.1 mol dm^{-3} , trivalent, Riedel-de Haën), KOH (0.1 mol dm^{-3} , trivalent, Riedel-de Haën) and standard buffers (Riedel-de Haën). The single crystal rutile (TiO_2) electrode was made using the single crystal ($10 \text{ mm} \times 10 \text{ mm}$, thickness 0.5 mm) obtained from MaTecK GmbH. TiO_2 is a semiconductor.¹⁶ The resistance of the used crystal was measured using U/I method of comparison with reference standard resistance of $1 \text{ G}\Omega$, and was approximately $5 \text{ G}\Omega$. The (0 0 1) plane was exposed to the electrolyte solution. The crystal surface was polished and cleaned with ethanol and redistilled water.

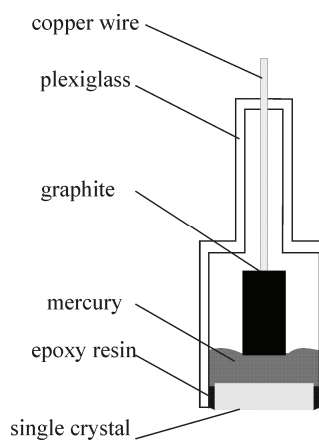


Figure 2. The single crystal rutile electrode for surface potential measurements.

An Ag|AgCl, Cl⁻(aq) electrode with a salt bridge (Metrohm, 6.0729.100) was used as a reference electrode. The salt bridge was filled with KNO₃ solution (0.1 mol dm⁻³).

Construction of the single crystal electrode is presented in Figure 2. The single crystal is fixed in the plexiglass holder with epoxy resin. Inner side of the crystal is in contact with mercury, and mercury is in contact with graphite connected to the copper wire. Outer side of the metal oxide single crystal is exposed to the electrolyte aqueous solution.

Acid-base Titrations. The system was thermostated at (25.0 ± 0.1) °C. The ionic strength was controlled with KNO₃. The solution (200 cm³) containing HNO₃ (10⁻⁴ mol dm⁻³) and KNO₃ (10⁻³ mol dm⁻³) was titrated with KOH solution (0.1 mol dm⁻³). At relatively low ionic strength it may be assumed that the point of zero charge does not deviate significantly from the isoelectric point, so that the latter may be used as the point of zero potential.¹⁷ In order to measure the SCrE potential as a function of pH, three electrodes were immersed: single crystal electrode (SCrE), Ag/AgCl, Cl⁻ reference electrode and combined Ag/AgCl, Cl⁻/glass electrode. To avoid mutual effects through the public electrical network, two pH-meters powered by batteries were used (Metrohm 826). The system was gently mixed with a magnetic stirrer.

RESULTS

Figure 3 demonstrates the measurement with the rutile electrode for original solution and for the first and second additions of the base. First, the original acidic

solution (pH = 4.04) was monitored in the direct mode; the reading from pH meter (D1) was 233.0 mV. Then, the counter voltage of 233.0 mV was adjusted and applied, and the reading in the HRCM mode was -2.8 mV. In the third step, the device was switched back to the direct mode and the D2 value was found to be 230.2 mV. The counter voltage of 233.0 mV was corrected for incomplete compensation (-2.8 mV) so that the SCrE electrode potential in the reversible condition was obtained as 230.2 mV. Scattering of the measured values was found to be within 1 mV and the readings were stable. After the first portion of the base (pH = 4.58), the SCrE potential was lowered so that D1 and D2 values were 208.1 and 206.2 mV, respectively. The HRCM value was obtained as 206.3 mV. The second portion showed similar behavior, but again the lower value of the SCrE potential was observed. It may be concluded that the direct mode and HRCM produce practically equal values, which is due to the fact that the pH meter employed in this study has sufficiently high internal resistance.

Figure 4 displays the effect of pH on the surface potential at the rutile (0 0 1) plane exposed to aqueous solution. The electrode potentials of SCrE were converted to surface potentials by setting the value of the surface potential ψ_0 to zero at the isoelectric point.¹⁷ For rutile (0 0 1) plane,¹⁸ $\text{pH}_{\text{iep}} \approx 5.7$.

As expected on the basis of the Surface Complexation Model,^{19,20} rutile exhibited almost linear dependency of surface potential on pH, with the slope being lower in magnitude compared to the Nernst equation. The slope is -50.97 mV, *i.e.*, 13.6 % lower than the Nernstian. The points measured directly with the pH-meter coincide with the data obtained by HRCM.

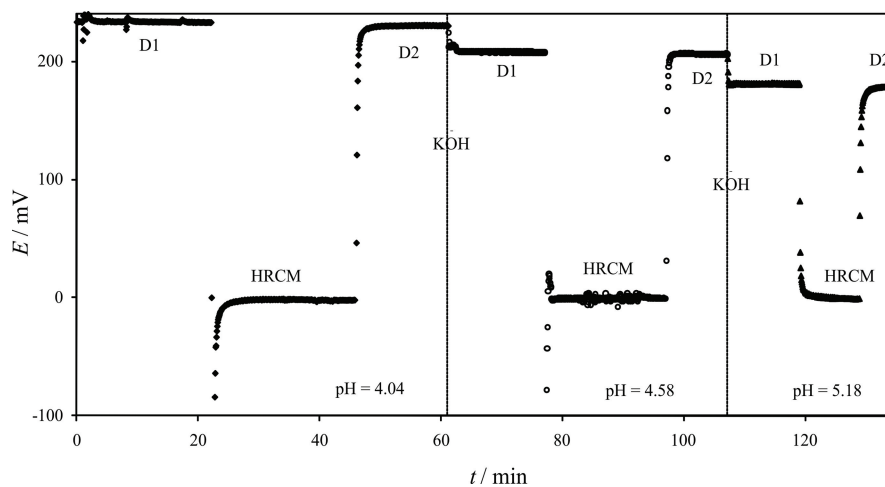


Figure 3. Acid-base titration with the rutile SCr electrode (original solution, and also for two additions of the base to acidic solution). Electrode potentials in the initial acidic solution (pH = 4.04), and after two additions (pH = 4.58 and pH = 5.18) were measured in the direct mode (D1), by the high resistance compensation method (HRCM), and again checked by the direct mode (D2).

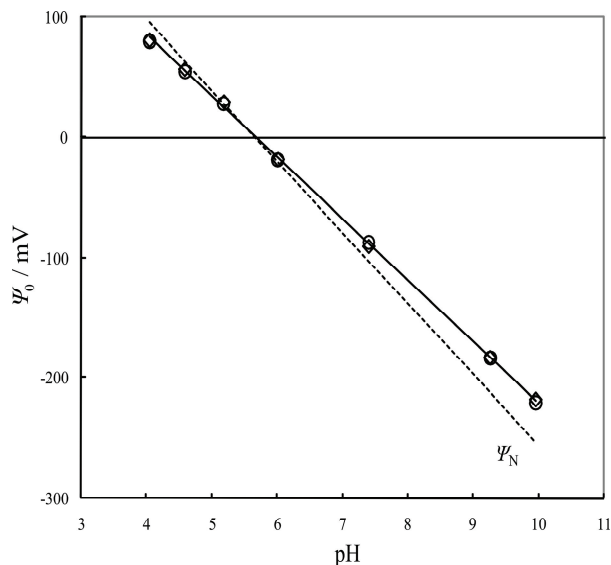


Figure 4. Surface potential (Ψ_0) of rutile (0 0 1) plane as a function of pH in aqueous KNO_3 solution ($I_c = 0.001 \text{ mol dm}^{-3}$) at 25°C , as measured directly with the pH-meter (\circ), and by HRCM (\diamond). The Nernstian potential (Ψ_N) is represented by the dashed line. Surface potential Ψ_0 was obtained from the measured electrode potentials taking into account the isoelectric point for rutile (0 0 1) plane¹⁸ $\text{pH}_{\text{iep}} \approx 5.7$.

DISCUSSION AND CONCLUSIONS

In this article, we have demonstrated the potential of the HRCM developed for measurements of electrode potentials of high-resistivity electrodes. This method is especially useful for measurements of surface potentials of crystal planes in contact with electrolyte solutions by means of single crystal electrodes. Even in the case when direct measurements using a high resistance millivoltmeter (pH-meter) produce reproducible results, one cannot be sure that the measured values are equilibrium values, *i.e.*, the values corresponding to equal rates of adsorption and desorption of ions at the interface. The high resistance compensation method solves the problems related to direct measurements, but also those associated with the classical compensation Poggendorff method. The method may be used for any source of the electric potential but is especially useful for evaluation of the surface potential at the solid/liquid interface since it enables characterization of specific crystal planes, which is important for interpretation based on the advanced MUSIC model.²¹ Most of the published data on charging the aqueous interfaces of crystals are obtained with colloid particles, thus yielding average properties

of all planes exposed to the liquid medium. Such average properties (electrokinetic potentials and surface charge densities) cannot be used for advanced theoretical treatments based on consideration of the specific structure of a defined crystal plane. In addition to advanced electrokinetic techniques, providing electrokinetic potentials of defined crystal planes,¹⁸ the corresponding surface potential data enable a better insight into interfacial equilibrium. It may be concluded that in order to ensure that data correspond to the equilibrium state at a specific crystal plane, the proposed High Resistance Compensation Method may serve as a useful tool.

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SAŽETAK

Visokootporna kompenzacijska metoda za mjerenje površinskih potencijala

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Razvijena je visokootporna kompenzacijska metoda (HRCM) za mjerenje elektrodnih potencijala viskootpornih elektroda. To je u osnovi klasična Poggendorffova kompenzacijska metoda, gdje je umjesto ampermetra, pH-metar uključen kao indikator potpune kompenzacije. Metoda je primijenjena za mjerenje elektrodnog potencijala elektrode s monokristalom rutila (TiO₂). Elektrodni potencijali su preračunati u površinske potencijale, te je određena ovisnost površinskog potencijala o pH u vodenom mediju.