USE OF MODIFIED CONDUCTOMETRIC METHOD FOR MEASUREMENT OF RESISTANCE OF COLLECTOR CORROSION LAYER

Pavel Abraham
Doctoral Degree Programme (1), FEEC BUT
E-mail: xabrah02@stud.feec.vutbr.cz

Supervised by: Petr Bača
E-mail: baca@feec.vutbr.cz

ABSTRACT

Conductometry is analytic method that can be used to analyze character of electrolyte. Conductometric measurement can be used also for resistance measurement of interface of electrode/electrolyte. This resistance corresponds with health of electrode and because resistance of corrosion layer is greater then resistance of electrode itself we can assume the corrosion rate from resistance of corrosion layer.

1. INTRODUCTION

Conductometry is analytic method that can be used to analyze character of electrolyte using measurement of the whole electrolyte conductivity. Every material participates in electric conductivity of electrolyte and we cannot recognize contribution to conductivity of each material. Thus conductometry is non selective analytic method that gives us information about total contents of materials in analyzed electrolyte.

The advantage of this method is that no electrochemical reaction (oxidation or reduction) occurs during measurement in the cell. We measure character of whole content of electrolyte between electrodes.

Electric current is related to moving electric charges - ions, these particles have permanent electric charge and they are moving to the negative (cations) and to positive (anions) electrode and also to polarization of molecules or dipoles orientation.

If neutral molecule is between electrodes, its inner negative charge is moving to the positive electrode and vice versa (electronic polarization) so the molecule has inducted electric dipole oriented in the direction of electric field.

Many non symmetric molecules have permanent electric dipole even without influence of electric field; if there is not an electric field present these permanent dipoles are randomly oriented in the electrolyte, but if there is electric field present then it orients dipoles (dipole polarization).

Electric charges move only in case of appearance or disappearance of polarization event – i.e. in case of appearance or disappearance off electric field or when its direction is changed. Time from appearance to disappearance of electric event is in μs, electric field should change with the similar speed.

During measurement of conductivity alternate current (A.C.) is used. Low frequency condumetry is used with frequency from 10^1 to 10^4 Hz and polarization events are not evident. Amount of current depends especially on change of particle concentrations with permanent electric charge, ions, and it doesn't depend much on frequency.

The advantage of high frequency conductometry (10^6 až 10^8 Hz) is in separation of contact between conduction electrodes and analyzed electrolyte.

When high frequencies are present, electromagnetic energy goes through walls of vessel, so conducting electrodes can be placed outside of the vessel, so they are not in direct contact with analyzed electrolyte. When high frequency alternate current is used in high frequency conductometry both components participate on total impedance equally, high frequency conductivity of electrolyte has complex character and it depends greatly on frequency of alternate current[5].

Analyzed electrolyte is during conductometric measurement in conducting (conductometric) vessel. To avoid polarization of electrodes, alternate current is leaded through electrodes. Conducting vessel shown at fig. 1 can be represented by electric circuit at fig. 2.

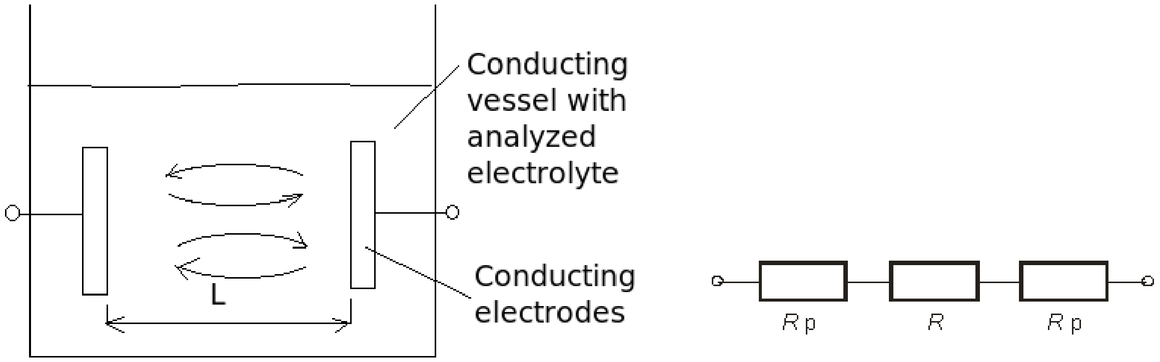

Fig. 1 and **2** Conducting vessel with electrodes, *R* is resistance of vessel and *Rp* is resistance of wires.

Conducting vessel has impedance character with capacitance component. Substitution diagram of real conducting vessel is more complex and it covers additional parts as it is shown in fig. 3.

When the electrode is inserted into the electrolyte chemical reactions occur that cause imbalance of charges. This imbalance is compensated by movement of charged ions to the electrode until imbalance is fully compensated. Near electrode there rises the double layer formed by charged ions and opposite charged electrode. This double layer acts as charged capacitor on certain potential [1,2]. Passing of charges through double layer is slowed by velocity of electron change between ions and electrode. This event has resistance character and it is called charge transfer resistance [1,2,3]. In the scheme there is represented by resistor R_{ct}. Z_w is Warburg's impedance and it is caused by limited diffusion velocity of ions from electrolyte to electrode [1,4]. Z_w and R_{ct} together makes Faraday's impedance that represent parasite behavior of cell together with parallel capacity C_{dl}.

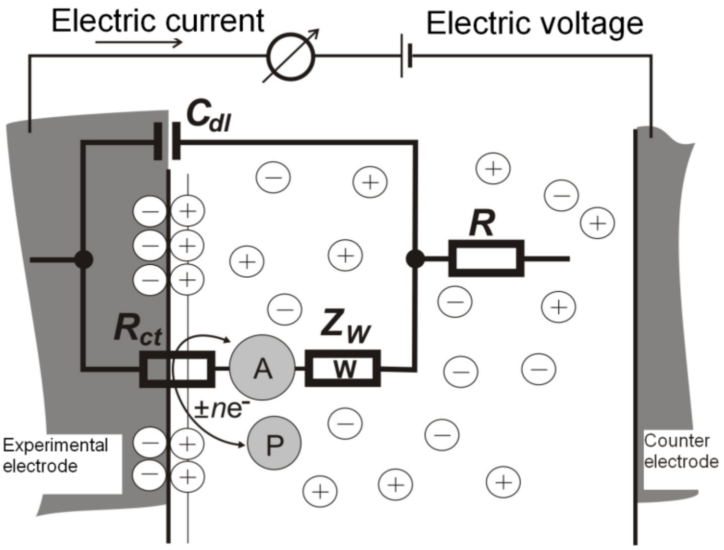

Fig. 3: Randles circuit of electrochemical cell (R - resistance of electrolyte, C_{dl} - capacity of double layer, R_{ct} - charge-transfer resistance, Z_w -Warburgs resistance [5].

In two-electrode configuration various layers can develop on electrodes, that contribute to the total resistance of vessel and also not completely compensated polarization of electrodes can occur. Size of current depends on total resistance in vessel i.e. not only on resistance of electrolyte, but also on health of electrodes and resistances of electrode/electrolyte. In the four-electrode configuration the current flows through one pair of electrodes and other pair is inserted between them. With the second pair of electrodes electric voltage with absence of current is measured. Measured voltage is not influenced by events on electrodes with current so it depends only on resistance of electrolyte.

You can see that four-electrode conductometric measurement can be used also for resistance measurement of interface of electrode/electrolyte. This resistance corresponds with health of electrode and because resistance of corrosion layer is greater then resistance of electrode itself we can assume the corrosion rate from resistance of corrosion layer.

Although primary use purpose of conductometric method is to measure conductivity of certain electrolyte and it needs inert electrodes (usually platinum electrodes), we can see from previous article, that conductometric method can be used as a comparative method for determination of corrosion rate of certain electrode system. This method can be used to find optimal composition of lead alloy for grid of positive electrode of lead acid accumulator, which is first destroyed by corrosion during exploitation in sulfuric acid. Also for development of bipolar lead-acid accumulator these results can be useful, because corrosion of bipolar substrate is one of failure mode of bipolar lead-acid accumulators. On this account bipolar lead-acid accumulators cannot be industry produced.

2. ANALYSIS

First of all we tried to verify functionality of conductometric method for resistance measurement of corrosion layer at the interface collector/electrolyte. We tried to determine how real and imaginary part of impedance depends on frequency and how it changes during time of measurement.

Experimental electrode was made from low-antimony lead alloy Pb Sb1,68 Sn0.05 (wt%). Individual ribs of electrode had dimensions 20x1 mm. Distance between ribs was 5.5 mm.

Before we start with experiment we made experimental cell, that contained excess of electrolyte and negative active material from industry produced negative electrode of starting battery from AKUMA a.s. Mladá Boleslav. Negative electrodes were placed on both sides 2.5 mm far from experimental positive electrode. No separator was used. For creation of corrosion layer we charged the electrode with 0.2 A for 120 hours.

To find out optimal frequency, when the imaginary part of impedance would be minimal we analyze voltage U_1, U_2, U_3 and its phase difference in whole frequency range of power source of sine signal. To analyze values we used two channel digital oscilloscope ALIGENT CN45004070. From measured voltages and its phase difference we calculated Z_{abs}, Z_{real} and Z_{imag}.

Fig. 5 shows imaginary part on the real part of impedance for electrolyte (i.e. Nynquist chart) and its substitution diagram. By measurement on whole system effect is similar, but you can see also Warburg impedance Z_w. From fig results: For measurement is better to use lower frequencies. Our power source had too much noise at 1 kHz frequency so we decide to measure at 5 kHz.

Sine generator was set to 5 kHz. And we tried to analyze time changes of absolute value of electrolyte impedance like in previous experiment. Fig. 6 shows how impedance depends on the time for system consist of experiment electrode and also negative counter electrodes. Error of measurement is not higher than 1.5 %. In system with experimental electrode only there is error of measurement to 0.7%. Measurement with negative electrodes is influenced by error so we decided to do next measurement without them.

Influence of negative electrodes is more significant by measurements of whole system in two-wires wiring. With negative electrodes the absolute impedance decreases stably. Without negative electrodes the absolute impedance is stable – 0.5 % deviation.

Measured value of absolute impedance is always lower in system with negative electrodes. It is caused by high conductivity of active mass of negative electrodes. So some current flows through negative electrodes and lower the absolute impedance.

2.1. FIGURES

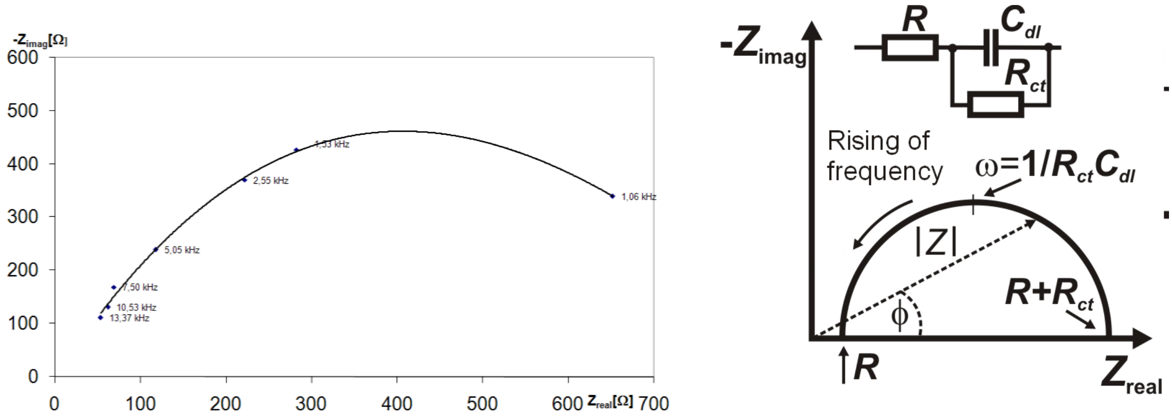

Fig 4,5: Dependency of imaginary part of electrolyte impedance on real part for various frequencies

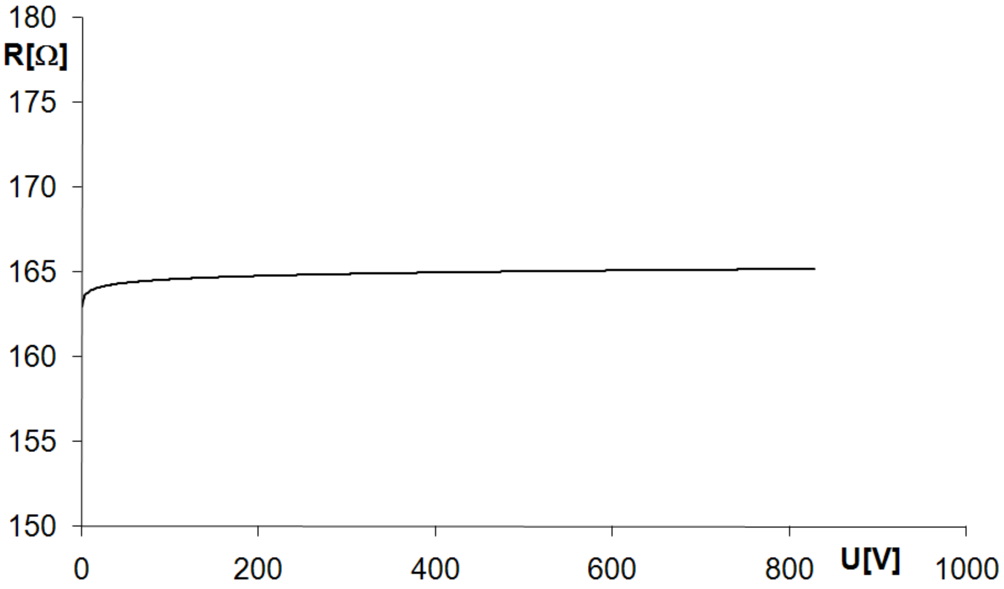

Fig 6: Time dependency of absolute impedance of electrolyte with negative electrodes

3. CONCLUSIONS

Our preliminary experiments shows that conductometric method is acceptable for resistance of corrosion layer measurement at interface electrode/electrolyte and it can be used as comparative method for measuring of various collector alloys to find out corrosion rate of that alloy.

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