

A facile route to temperature determination in hot-wire electrochemistry

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Abstract The determination of the actual electrode surface temperature is important for all electrochemical methods using in situ heating of electrodes. Existing methods of temperature measurement of a heated thin-wire electrode are of restricted use and critically discussed in the introduction. The use of the electrode wire itself as a resistive thermometer is improved in the present method. With the new thermoelectrochemical method temperature pulse voltammetry, the reliability of different thermometric methods can be compared. In this way, it is ensured to have correct temperature measurements at wire microelectrodes in all common solvents available.

Keywords Modern thermoelectrochemistry · Heated wire electrode · Cyclic voltammetry · Temperature pulse voltammetry · Open circuit potentiometry

Introduction

Hot-wire electrochemistry, i.e., working with thin wire electrodes that are heated in situ by power AC current, is a prominent technique among modern thermoelectrochemical methods. It is meaningful for solid state electrochemistry, since it assigns solid electrodes with properties which are

otherwise typical for the classical mercury drop electrode. Such features are, e.g., a well-reproducible stirring effect, and the chance to renew an electrode surface by in situ thermal treatment.

Modern thermoelectrochemistry is characterized by a new concept regarding the role of temperature. In the new methods developed during the last decades, temperature changes are applied as an independent variable [1], like, e.g., light in photoelectrochemistry. This means that electrode surface temperature has to be varied fast and arbitrarily. In practice, the electrode or a region near the electrode is heated in the course of an electrochemical experiment. Well-known thermoelectrochemical methods are the technique discussed here [2], or, as a further example, microwave heating of a tiny solution spot near the surface of a microelectrode [3].

In electrochemical techniques using electrode heating, a temperature gradient between electrode surface and the bulk of solution is formed. A metallic electrode body itself, however, can be assumed to be of uniform temperature, if thin wire electrodes are heated. At the solution side, the place with maximum temperature is the electrode surface. Exact value of its temperature as well as the time dependence of the latter is highly important. Temperature measurement, however, is not trivial with tiny wires or solution spots. For heated wire electrodes, a number of temperature determination methods have been developed during the last years. Some of them will be discussed here. A new route to follow the temperature change of heated microwire electrodes based on modern thermoelectrochemical methods will be presented.

Besides calculation of temperature, there exist two principal ways to determine the surface temperature of heated thin wire electrodes. A wire diameter of 25 μm is assumed in all considerations.

Dedicated to Prof. Dr. Fritz Pragst on the occasion of his 70th birthday.

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Techniques most successfully used in thin-wire temperature measurements are the following:

1. Open circuit potential (OCP).

The electrode is heated in a solution containing both components of a reversible redox couple, e.g., an equimolar mixture of ferricyanide and ferrocyanide. The redox couple used should be characterized by a high reaction entropy, i.e., its standard electrode potential has a large temperature coefficient. By following the open circuit potential change, the temperature as a function of time can be recorded with heating and cooling processes.

2. The electrode wire itself is used as a resistive thermometer.

Electrode resistance can be measured in the course of heating with a stabilized heating current, or alternatively a stabilized heating voltage, when simultaneously the corresponding voltage and current, respectively, is recorded. With this method, continuous temperature changes can be followed, similar to method 1.

The advantages and disadvantages of both techniques are as follows:

OCP measurement is applicable only for a reversible redox couple which should have two stable and substantially available redox partners besides the high entropy value. Frequently, the second condition is a problem for redox couples in non-aqueous solvents. It would be helpful if the electrode temperature could be determined applying only one partner of a redox couple. Furthermore, there are large uncertainties about the numerical value of the redox entropy. Numerous values are given in the literature for aqueous solutions as well as for a large variety of non-aqueous solution compositions. In most cases, temperature dependence of voltammetric half-wave potential has been the basis for entropy determination. The extent of uncertainty can be illustrated by considering the values given for ferrocene in acetonitrile [4–7]. Variation of dE/dT was found to vary between 0.4 and 0.8 mV/K.

Resistivity of the wire as a source of temperature changes is restricted to very thin wires in the micrometer range. Otherwise, thermal inertia of the material would prevent reliable indication of fast changes. Wires (25 μm) gave no problems.

A second problem with the “electrode body thermometer” is its integral resistance signal, i.e., the whole wire segment between galvanic contacts acts as a source of thermal information, including the parts covered by insulating material. These parts may assume a temperature somewhat different from the part exposed to solution. The covered wire segments may be heated up to a somewhat higher temperature since they are insulated thermally. On

the other hand, these parts are always close to electric contacts. The latter may cause some cooling, if they consist of larger metallic structures. In other words, the electrode surface temperature determined by resistivity measurements can be considered as some kind of the average temperature of the wire segment between the electric contacts. This is the reason for an unprecisely predicted sign of the resulting thermal non-uniformities.

The new electrochemical method described in this paper circumvents the drawbacks of established methods in the determination of electrode temperature. Thus, a realistic validation of all existing in situ techniques is possible.

Experimental

Chemicals

Aqueous solutions were prepared with double distilled water. Acetonitrile (Sigma-Aldrich) of highest available purity was used after permanent storage over molecular sieve 0.3 nm (Merck). All solutions were purged with pure nitrogen prior to electrochemical experiments.

Potassium chloride (Merck), potassium ferrocyanide and ferricyanide (both Sigma-Aldrich), and ferrocene (Merck) were used in the highest available purity grade without further purification. Tetrabutyl ammonium hexafluorophosphate (Fluka) had been dried at 80°C in a vacuum oven and stored over calcium chloride.

Apparatus and cells

All electrochemical measurements and also the precision resistance determination of platinum wires were done with the potentiostat HEKA PG390 (HEKA Elektronik Dr. Schulze GmbH, Germany) in combination with the software package *Potmaster PG390*. The potentiostat is connected to a home-built instrument designed for heating an electrode wire in situ by AC [8]. In brief, this instrument contains a 100-kHz AC generator, an AC power amplifier, and a special transformer. The electrode is connected with the transformer secondary winding output via a bridge configuration containing two inductive coils. The heating process is triggered by feeding a TTL trigger signal from potentiostat to the trigger input of the home-built instrument. A wiring diagram of the equipment is given in Fig. 1. In all of the experiments described below, a heating voltage of 1.895 V root mean square (rms) was imposed. This value was known to generate a medium temperature at the Pt wire used here.

The basic electrode design has been published elsewhere [9]. Briefly, a platinum wire 25 μm in diameter is soldered between copper leads on a printed board support. Contacts and copper conductors are insulated by laminating foil

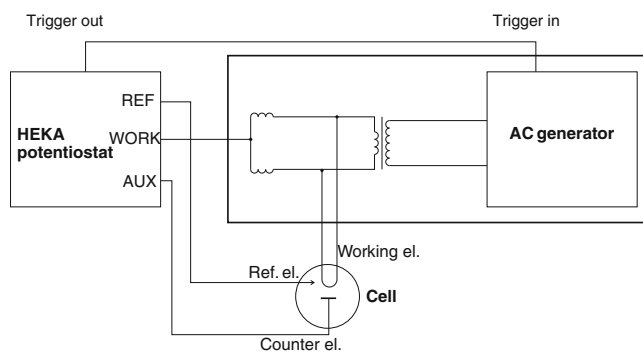


Fig. 1 Wiring diagram showing connections between potentiostat, electrolysis cell and 100 kHz AC heating unit. Working electrode was a 25 μm platinum wire of ca. 24 mm in length

carrying a hot glue layer. In the improved electrode version used here, at the opposite side of the printed board support, additional electrodes are placed. These were made of copper conductors plated by gold (to form a counter electrode) or by a silver layer which was chloridized to form a pseudo reference electrode.

For all electrochemical experiments, an electrochemical mini-cell was used. It consists of a thick-walled test tube of 10 ml volume closed by a special PTFE cap with holes for cannulae acting as nitrogen in- and outlets. The cap also fixes the electrode strip. Cap and electrode strip were tightened hermetically by silicon rubber sleeves in a way that free contact to atmosphere was by the nitrogen outlet. In experiments with acetonitrile solution, a small amount of 0.3 nm molecular sieve beads was added to the cell. Electrolyte volume was generally 5.0 ml. With acetonitrile, an on-board pseudo reference electrode was used. In measurements with the ferri/ferrocyanide redox couple, other reference electrodes were preferred. In solutions containing both components of the redox system, a non-heated platinum wire was sufficient to act as a reference electrode. In studies where only ferricyanide was studied, a classical saturated Ag/AgCl electrode was inserted. In ferri/ferrocyanide solutions, an additional platinum wire was used as a counter electrode instead the on-board gold strip. For in situ resistivity measurements, the electrode strip was placed in a 50-ml cell to avoid partial heating of the solution. For calorimetric calibration, the mini-cell described above was placed in a dewar chamber made of polystyrene foam.

Procedures

Open circuit potential (OCP) measurements were performed with the heat-treated electrode described above in an aqueous solution containing potassium ferricyanide and potassium ferrocyanide in equal concentration (normally 2 mM each) with 0.1 M KCl. In a initial period of 0.1 s, the open circuit potential of the electrode wire was recorded

without heating. Heating process was triggered afterwards with a duration of 10 s. For further 10 s, heating was switched off. Electrode potential was recorded continuously over all the mentioned three periods.

Cyclic voltammetry (CV) studies were performed in a three electrode configuration using a potentiostat with the only exception that in electrode heating experiments, the heating process was started by a trigger signal 0.1 s before CV recording. The scan rate was 50 mV/s throughout all experiments.

Temperature pulse voltammetry (TPV) experiments followed the general scheme given elsewhere [10]. TPV signals are current values sampled close to the end of a heating period during a potentiostatic electrolysis. Here, n sweeps were performed each belonging to a selected potential value. Each sweep consisted of three sequences. In a first sequence of 0.1 s, no heating was applied. In the next sequence, without changing the potential, the heating process was started and continued for 10 s. During the last 10% of this heating period, the electrolysis current value was measured and averaged. The resulting current value is representative for one point of the “hot” TPV curve. During the next sequence of 10 s, heat was turned off and current was sampled during the last 10% as in the second sequence. The resulting value gives one point in the “cold” TPV curve. The three-sequence sweeps were repeated n times with a new potential value for each sweep. This way, n points were obtained to form the TPV curves. Potential increase from one sweep to the next was 10 mV.

Resistance of the electrode wire was determined by the potentiostat with the outputs for reference and counter electrodes short-circuited. The electrode wire was connected to the resulting output and that of the working electrode. The electrode was placed in a cell containing 50 ml of pure water. In a potentiostatic sweep, the electrode wire remained unheated during a short sequence of 0.1 s. In the next sequence of 10 s, a DC heating voltage of 1.895 V was applied to the wire followed by an unheated sequence of 10 s. During this sequence, a voltage of 100 mV was imposed. During sequences 2 and 3, the actual current as well as voltage values were recorded continuously. The actual temperature-dependent resistance of the wire during heating (and cooling, respectively) was calculated from actual current and voltage values. By means of the well-known temperature dependence of platinum resistivity, the actual temperature changes could be calculated, as pointed out in the next paragraph.

The applied voltage of 1.895 V was chosen to correspond to the rms value of AC heating voltage used here. Since there was some doubt whether AC and DC voltages of similar magnitude indeed would bring about equal heat effects, their efficiency was compared by means of a calorimetric experiment. The described mini-cell,

equipped with the heated wire platinum electrode and filled with 5 ml water, was placed in a thermally isolating foam case forming a simple calorimeter. The electrode was heated for longer time (minimum 10 min), either with AC or with DC of formal equal magnitude of 1.895 V. Before and after this heating period, the electrode wire resistance was measured as given above. When small temperature changes during pre- and after-heating periods were considered carefully, a good agreement of AC and DC heating results is found. Deviations are less than 1% for 1.895 V.

Results and discussion

In a solution containing ferri- and ferrocyanides of equal concentration, even cyclic voltammograms with and without permanent heating show a marked temperature dependence as illustrated in Fig. 2. With electrode heating, not only the electrolysis current values tend to increase, but also the shape of the voltammogram changes towards a sigmoidal appearance. These alterations are induced by the increase of the diffusion coefficient and also by a thermal stirring effect which tends to decrease the thickness of actual diffusion layer. Both types of voltammogram allow the determination of the actual half-wave potential in the usual way. With the applied heating AC current at 1.895 V_{rms}, the temperature-dependent potential shift gives a temperature increase of 32.6 K. It has been calculated using a temperature coefficient of 1.6 mV/K [11]. Unfortunately, a more precise value of the heating time cannot be given for CV. Otherwise, CV with permanent heating is not really useful for temperature determination. Nevertheless, a rough estimation of ΔT is possible. This is a valuable feature since the potential shift could be evaluated also with

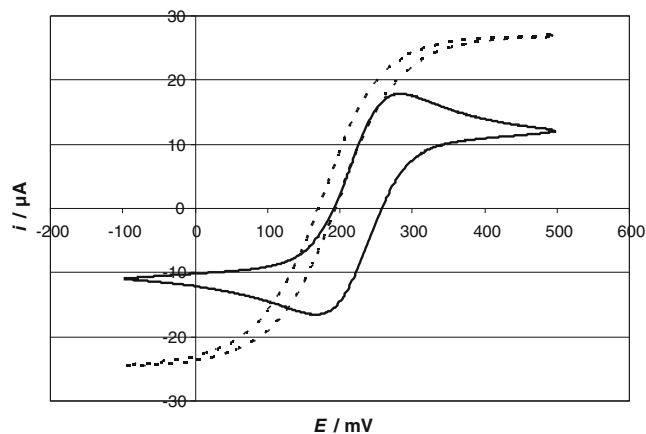


Fig. 2 Cyclic voltammograms of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ (2 mM each) in 0.1 M KCl. Scan rate 50 mV/s. *Solid line*: without heating, *dotted line*: permanent heating by a voltage of 1.985 V_{rms}. Platinum wire electrode 25 μ m in diameter

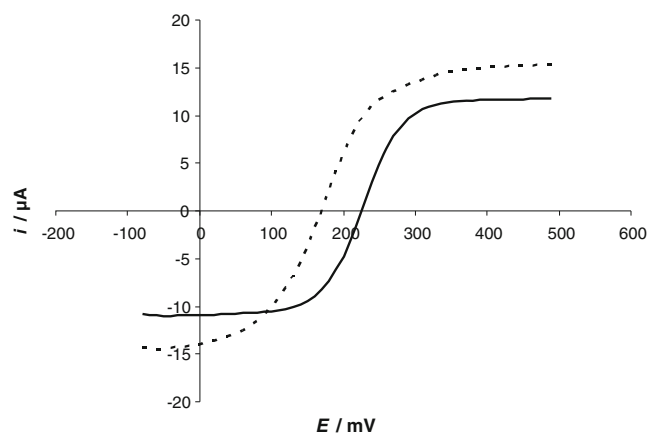


Fig. 3 Temperature pulse voltammograms (TPV) of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ (2 mM each) in 0.1 M KCl. *Solid line*: Current at the end of 10 s cooling-down period (cold curve). *Dotted line*: Current at the end of 10 s heating-up period (hot curve). Heating with 1.895 V_{rms}. Platinum wire electrode 25 μ m in diameter

a solution containing only one of the redox couple partners, e.g., with ferricyanide alone.

Temperature pulse voltammograms (TPV) of ferri/ferrocyanide 2 mM each are given in Fig. 3. In contrast to CV, TPV results provide information about actual temperature for every instant of heating-up and cooling-down periods. In the example given, for 0.5 s after heating has started, an actual temperature increase of $\Delta T=31.4$ K has been calculated from half-wave potential shift using $dE/dT=1.6$ mV/K [11]. After 10 s of heating, $\Delta T=32.6$ K was attained. This value corresponds to that estimated with CV. With TPV, however, the heating time is well defined, and the precision is much higher than with CV since no graphical evaluation is necessary. The heating period has been extended to longer

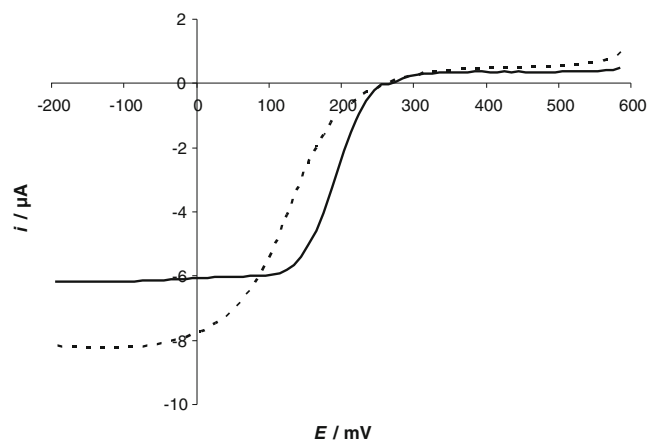


Fig. 4 Temperature pulse voltammogram (TPV) of 2 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl. *Solid line*: current at the end of a 10 s cooling period (cold curve). *Dotted line*: current at the end of 10 s heating period. Heating, 1.895 V_{rms}. Platinum wire electrode of 25 μ m in diameter

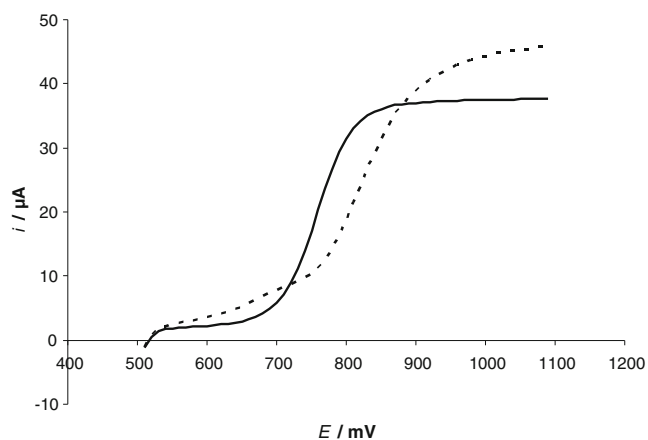


Fig. 5 Temperature pulse voltammogram of a 2-mM ferrocene/ acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate. Heating, 1.895 V_{rms}. Platinum wire electrode of 25 μm in diameter

times. After ca. 30 s, a constant value was approached with ΔT=32.3 K.

Figure 4 shows TPV of a solution containing ferricyanide only. The results are well consistent with those of ferri/ferrocyanide mixtures. For 0.5 s, ΔT=31.2 K, for 10 s, 32.4 K, and for infinite time, 32.5 K are estimated. The results show clearly that TPV can provide temperature values with only one part of a redox couple, i.e., with easily accessible substances.

In Fig. 5, a 2-mM ferrocene solution in acetonitrile has been studied by TPV. The temperature coefficient of the ferrocene electrode potential is low in most common solvents. For acetonitrile solutions with 0.1 M NBu₄PF₆ as supporting electrolyte, literature values of ΔE_{1/2}/ΔT range between 0.4 and 0.8 mV/K. We have re-determined the value following the procedure given by Akkermans et al. [6] and found 0.8 mV/K. The value is low but just sufficient to estimate the temperature increase by heating with a voltage of 1.895 V_{rms}. As a result, ΔT=56.0 K was

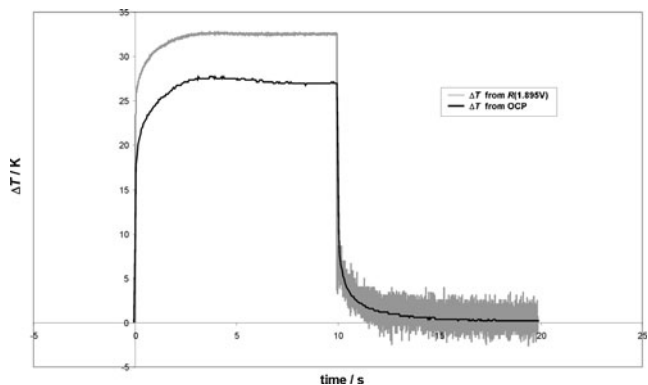


Fig. 6 Temperature changes during and after a 10-s heating pulse. ΔT values measured by OCP (black line) and by resistivity evaluation (gray line). Heating voltage 1.895 V_{rms} for AC heating and 1.895 V_{dc} for DC heating

Table 1 Temperature rise within the indicated pulse, caused by heating a Pt wire electrode with U=1.895 V, measured by cyclic voltammetry (CV), by temperature pulse voltammetry (TPV), by evaluation of resistivity change (R det.), and by open circuit voltammetry in a ferri/ferrocyanide solution (further explanation see text)

Method	ΔT (0.5 s)/K	ΔT (10 s)/K	ΔT (t→∞)/K
CV	–	–	32.6
TPV with K ₃ /K ₄ [Fe(CN) ₆]	31.4	32.6	32.3
TPV with [Fe(CN) ₆]	31.2	32.4	32.5
R det.	31.6	32.6	32.6
OCP with K ₃ /K ₄ [Fe(CN) ₆]	22.7	27.2	31.9

calculated. Apparently, acetonitrile is heated to a higher degree compared to water when equal heating current is applied, due to its lower heat capacity and thermal conductivity.

Those methods are of special interest, which allow a determination of the temperature change as a time function in the course of heating or cooling processes. TPV does not provide a continuous signal, but open circuit potential measurements can be used to follow dynamic processes. Till now, this was the reason to prefer OCP and to establish it as a reference method in hot-wire electrochemistry. On the other hand, continuous tracking of temperature during dynamic processes in non-aqueous solvents is required where no redox couples possessing favorable properties like ferri/ferrocyanide in water are available. This was the reason to reconsider a well-established technique where heated platinum wires were used as a resistivity thermometer [12]. Unfortunately, temperature values obtained by OCP proved to be rather different from such obtained by evaluation of R = f(T). It seemed that the discrepancy could not only be ascribed to the differences in measuring principles (integral with R, only

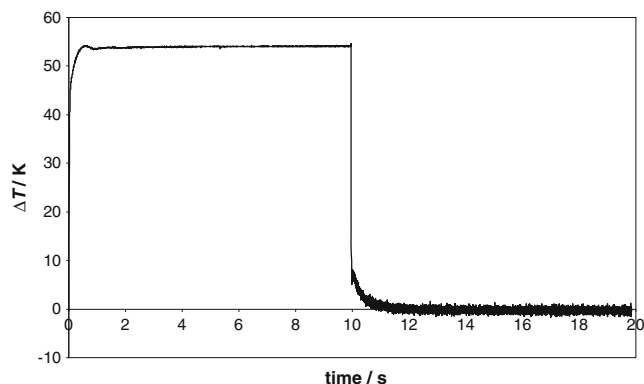


Fig. 7 ΔT values measured by resistivity evaluation in acetonitrile. Heating voltage 1.895 V_{dc}. Electrode body is identical to that used in all experiments in aqueous solution

exposed surface temperature with OCP). Therefore, TPV was considered as a third reference method. In Fig. 6, results are compared for heating and cooling processes of an electrode studied by OCP and R measurement, respectively. For OCP, the electrode is heated by a voltage of 1.895 V_{rms} in a solution of K₃[Fe(CN)₆] and K₄[Fe(CN)₆], each 2 mM, containing 0.1 M KCl as supporting electrolyte. In resistance measurements, the same electrode was heated in water by a DC voltage of 1.895 V. OCP measurements were done as described in experimental section. For R measurement, the electrode was left unheated for 0.1 s, then a 10-s pulse for AC heating was applied, and with further 10 s, a DC voltage of 100 mV was applied. From the recorded voltage and current values, the resistance of the Pt wire was calculated as a function of time. The resistance value determined by averaging the last 10% of the sequence without heating was used as a reference value (R_{ref}). ΔT values were calculated by Eq. (1):

$$R_T = R_{ref}(1 + \beta\Delta T) \quad (1)$$

with $\beta=0.0038 \text{ K}^{-1}$.

Figure 6 shows a non-acceptable difference between OCP and resistive thermometer results. All results of the different temperature determinations are summarized in Table 1. Voltammetric values (CV and TPV) agree well with those from resistance measurements. It is remarkable that the ΔT value obtained from OCP after “infinite” waiting time (i.e., after ≥ 10 min) approaches the results of voltammetry and resistance measurements. Thus, the only explanation for discrepancies is the inertia of open circuit potential establishment. It is well known that in classical potentiometric studies at solid metallic electrodes, waiting times of some minutes are advantageous even with reversible redox couples to get stable OCP results. Obviously, the potential does not establish much faster if the surface temperature is increased to the extent discussed here. Processes at electrodes under current conditions proceed much faster.

The resistive method of temperature determination is applicable to all common solvents. This is demonstrated by Fig. 7, where the electrode used for studies in water is heated in acetonitrile with a voltage of 1.895 V, the same value applied in water. The measured temperature is very close to boiling point of acetonitrile. Indeed, first signs of boiling are visible depending on the actual room temperature.

Conclusions

Temperature values of heated platinum microwire electrodes can be measured in situ by means of temperature pulse voltammetry (TPV) in solution using reversible redox couples with only one partner of the redox couple and following the temperature-dependent wire resistance. Resistivity measurements visualize the electrode temperature as time function. Results of voltammetric and resistive measurements give similar results, although the electrode parts contributing to the temperature values are different in both methods. Experimental methods based on resistance determination are advantageous as they can be used in all common solvents.

Although open circuit potential measurements give continuous temperature values, the results do not agree well with those of resistive and voltammetric measurements. The reason of this disagreement is a sluggish response of open circuit potentiometry.

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