

The impedance-titrator : A novel setup to perform automated pH-dependent electrochemical experiments

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A new device for performing electrochemical experiments under automatic change or control of the solution pH was developed. The electrochemical cell consists of a thermostatted glass cell, counter electrode, reference electrode and working electrode, pH sensor, stirrer and gas purging system. A control box and a potentiostat equipped with a frequency response analyser form the electronic equipment, while a piston buret allows dosing the solution of interest e.g. a sodium hydroxide solution. Various modes are available for scanning the pH range or keeping the pH constant if a hydroxide consuming reaction shall be observed at a constant pH value, all during electrochemical experiments are performed. Two application examples are given to demonstrate the versatility of the impedance titrator. One addresses the determination of the breakdown pH value of anodised aluminium and the other quantifies the consumption of zinc during transient formation of zincate precipitates.

1 Introduction

The stability of metals in aqueous solutions is primarily dependent on the pH value. Some metals are prone to acidic dissolution, some metals dissolve easily under alkaline conditions. Those dissolving under either of these conditions are called amphoteric. Prominent examples are aluminium and zinc. The corrosion stability of a metal depends significantly on this property. The pH value of a bulk solution is either determined by its initial composition, e.g. for an alkaline or acidic medium, or results from the reaction of a metal with the surrounding electrolyte. It is therefore of vital interest to know the susceptibility of a material against a certain pH value. *Rückert* investigated the influence of the pH value of cold drinking water on the corrosion behaviour of galvanised steel tubes [1]. He characterised the surface layer forming at pH values higher than 7.9. Even metals like titanium, which are seen as corrosion resistant can corrode under special conditions. Like in fluoride containing electrolytes, even here the pH value plays an important role [2]. Related alloys such as shape memory alloy NiTi benefit from the corrosion resistance of its parent metal titanium but can be attacked under severe conditions requiring surface treatment [3]. On the other hand, a certain pH value can be used to initiate the precipitation of a protective layer. This deposition can be either irreversible, for example when a hydroxide precipitate converts into an oxide or can be sufficiently protective from the over all amount of material deposited. *Elias*

and *Srithar* studied the electrocrystallisation of hydroxyapatite on titanium as a function of the solution pH [4]. Other researchers namely *Schiller* and *Epple* demonstrated that pH fillers are useful additives [5]. This idea can be extended into self healing coatings for corrosion protection of metals. The basic idea is using encapsulated inhibitors, which are released upon reaching a critical pH value that triggers destruction of the capsule [6]. This pH change into alkaline values may be a result of an ongoing oxygen reduction underneath a coating or within a confined volume such as a flange.

The development of new materials or alloys for coating applications with increased corrosion stability under alkaline conditions would require a setup that allows an efficient determination of the materials stability under systematic change of the pH. The aim of this work is to introduce such a device that allows not only measuring the open circuit potential of a material in a certain solution but also allows for a systematic change of the pH value for scanning the range of interest or maintaining the pH during a reaction. In addition a comprehensive impedance spectroscopic characterisation is possible with this setup.

The functionality of that device will be illustrated by two examples. Monitoring of the pH dependent stability by means of impedance spectroscopy for aluminium was chosen as the first example [7]. An active regulation modus is exemplified for the coupled complex formation of various zincate species [8].

2 Experimental

The core idea of this paper is the development of a new experimental setup. Most of the experimental details are therefore given in the results and discussion section.

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2.1 Chemicals

All experiments were performed in sodium hydroxide solution (Titrisol $c = 1 \text{ mol} \cdot \text{l}^{-1}$, Merck; Darmstadt, Germany), diluted with purified water (behropur b5 purifier, Behr-Labortechnik; Düsseldorf, Germany). Zinc with a purity of 99.99% (Goodfellow; Cambridge, Great Britain) and aluminium (p.a., Merck; Darmstadt, Germany) was used. The reference electrode was a commercial LL ISE (Metrohm AG; Herisau, Switzerland).

2.2 Electronics

Electrochemical experiments were performed by an Ivium CompactStat (Ivium Technologies; Eindhoven, The Netherlands). The piston buret used was a Titronic Universal (Schott-Geräte GmbH; Ludwigshafen, Germany). Analogue signals were digitalised with a NI USB 6009 I/O box (National Instruments; Austin, TX, USA). The pH value was measured using a pH glass electrode (Unitrode), in combination with a pH-meter E 632 (both from Metrohm AG; Herisau, Switzerland).

3 Results and discussion

3.1 Experimental Setup

Figure 1 shows a schematic of the impedance titrator. The main part of this setup is an electrochemical cell which is equipped with a commercial $\text{Ag}|\text{AgCl}$ -reference electrode, a gold wire as counter electrode and the working electrode in a specially designed sample holder. To determine the pH-value, a pH-glass electrode is connected to a pH-meter. Its analogue signal undergoes a conversion using an analogue to digital converter (ADC) in a commercial USB-I/O-Box and the data are stored in a computer. The pH-glass electrode is combined with a built in Pt 1000 temperature sensor. In order to change the pH to more alkaline values, a piston buret, filled with a sodium hydroxide solution, which is also controlled by the computer, is connected to the cell. All electrodes and inlets are mounted in the cap of the cell, to guarantee a defined start of the experiment by a simultaneous immersion of all electrodes into the electrolyte. Digital I/O channels of the USB-I/O-Box are used to switch a gas valve, to purge the solution and a magnetic stirrer, which is mounted in the holder of the cell. Electrochemical experiments are performed by using an Ivium CompactStat. A self written LabVIEW Program allows controlling all functions of the impedance-titrator and recording of all measured data namely pH-value, temperature, added amount of solution, open circuit potential and electrochemical impedance spectra.

3.2 LabVIEW Program

The LabVIEW Program provides different measuring methods. An electrochemical experiment can be performed at different, user defined and automatically set pH-values. Another method is to repeat measurements in a user defined fashion. This can be either a simple monitoring as described in Section 3.3.1 or an active regulation of the pH value as explained in Section 3.3.2.

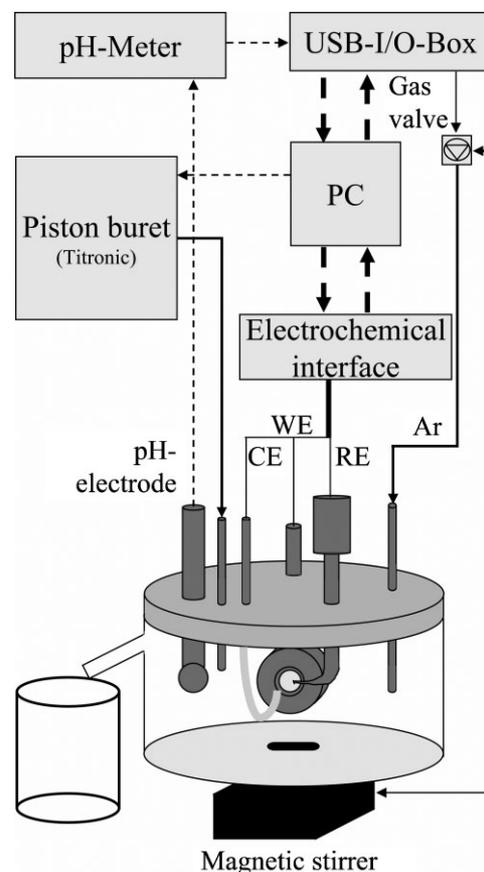


Figure 1. The impedance titrator: A schematic of the experimental setup

Prior to the electrochemical experiment a log file is created that contains date, time, temperature, pH-value and added amount of solution.

3.3 Electrochemical experiments

3.3.1 Transient electrochemical experiments with pH monitoring

The impedance titrator allows performing all electrochemical experiments provided by the Ivium CompactStat. These experiments can be performed in a sequence, with a user defined waiting time.

Before the electrochemical experiment is triggered a log file containing date, time, temperature, pH-value will be created. If the experiment takes more time than the user defined for the sequence-time, the next experiment will be triggered after the previous has finished.

3.3.2 pH-Scan

Figure 2 shows the flowchart of the subroutine, which will set user defined pH-values and initialise electrochemical measurements. Starting with the first pH-value, the subroutine calculates the volume of sodium hydroxide solution which is required to approach the next defined pH-value. This calculation takes into account the current pH-value, the concentration of the sodium

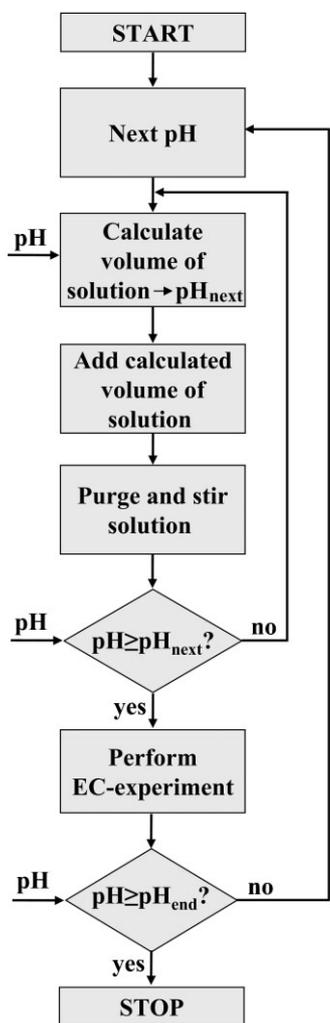


Figure 2. Flowchart for pH scan subroutine

hydroxide solution in the buret and the present electrolyte volume in the electrochemical cell. Then, the piston buret adds 95% of the required volume to avoid overtitration. Subsequently, the electrolyte is purged for 5 s and stirred for 8 s. If the electrolyte has not reached the target pH-value, the subroutine will calculate again the required volume of sodium hydroxide solution, using the new current pH-value. In this way a successive approximation of the target pH-value is achieved. Once the electrolyte has reached the defined pH-value (or the calculation yields a volume smaller than 0.01 ml) the electrochemical measurement will be triggered. The next defined pH-value will be set after finishing the electrochemical measurement. The subroutine will stop once the electrochemical measurement at the last defined pH-value is initialised.

3.4 Active pH regulation

Figure 3 shows the flowchart of the subroutine which allows performing electrochemical experiments at a constant pH-value, even if OH^- -ions from the solution are consumed by a reaction. The current pH-value of the electrolyte is kept constant within

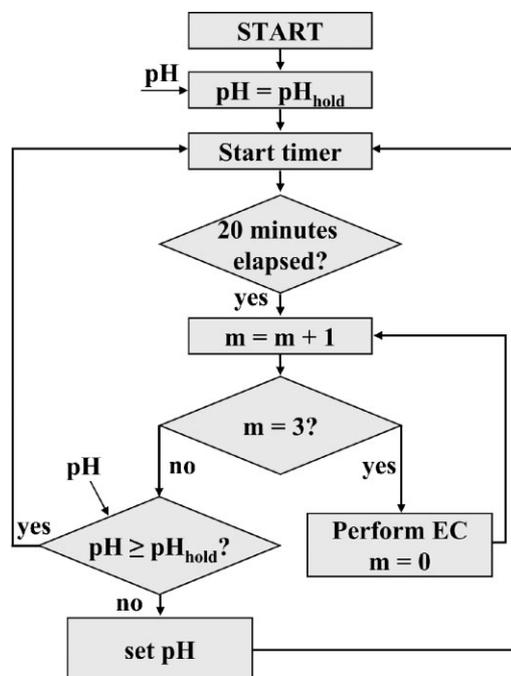


Figure 3. Flowchart for the active regulation subroutine

this subroutine. Every 20 min the pH-value of the electrolyte is checked and, if necessary, corrected by adding a supplemental amount of sodium hydroxide solution. Every hour the foreseen electrochemical experiment will be performed. The subroutine will run until the user pushes the STOP-button.

3.5 Constant pH-value

An electrochemical experiment was performed at a constant pH-value of 12.6 for 32 h. The development of the pH-value and the automatically added amount of sodium hydroxide solution to hold the pH-value constant are shown in Figure 4. Hydroxide ions were consumed by the corrosion of the zinc electrode. The pH-value was adjusted every 20 min.

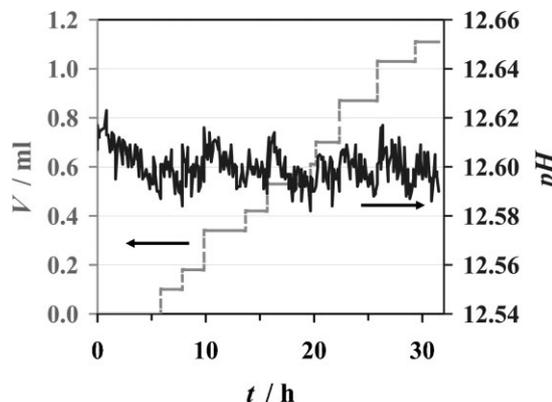


Figure 4. Development of the pH-value and the added amount of sodium hydroxide solution for an experiment at a constant pH-value, using the active regulation mode

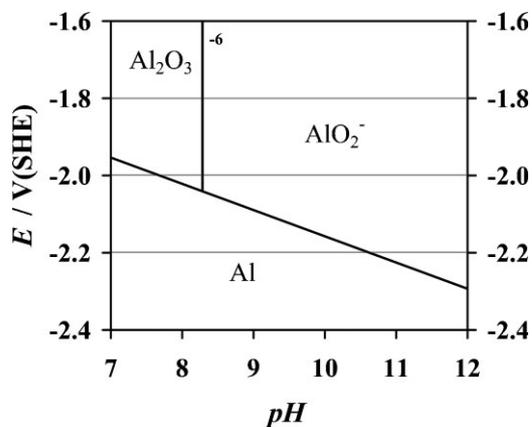


Figure 5. Simplified Al-Pourbaix diagram for a pH-range from 7 to 12 and an AlO_2^- concentration of $10^{-6} \text{ mol} \cdot \text{l}^{-1}$

After a first peak, the fluctuation of pH-value is less than ± 0.02 pH. The averaged pH-value over 32 h is 12.604. The addition of 1 ml sodium hydroxide solution yields at this pH-range an increase of 0.01 pH-units. The consumption of sodium hydroxide solution, the duration of the experiment and the sample size yield a calculated corrosion rate of $0.056 \text{ mol} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$.

3.6 Automatic determination of the breakdown pH-value of an anodic oxide layer on aluminium

Electrochemically grown oxide on aluminium is theoretically stable up to a pH-value of 8.5, if the electrolyte is nearly free of aluminium ions [9]. A simplified Al-Pourbaix diagram is shown in Figure 5. Using the impedance-titrator, the pH-dependent stability of an electrochemically grown aluminium oxide layer was investigated between $\text{pH} = 8.25$ and 9.5, with a step width of 0.25 pH. At each pH-value, the open circuit potential was recorded for 60 s and an electrochemical impedance spectrum between 10^3 and 10^{-1} Hz at five frequencies per decade was performed. The impedance spectra were fitted with a simple R-(RC) equivalent circuit. Figure 6 shows the resistance and the capacity of the sample with increasing pH-value. The resistance of the sample decreases from $168 \text{ k}\Omega \cdot \text{cm}^{-2}$ at a pH-value of 8.25 to less than $5 \text{ k}\Omega \cdot \text{cm}^{-2}$ at a pH-value of 8.75. At a further increased pH the oxide layer is no longer stable. The capacitive value of the sample decreases simultaneously with increasing pH-value.

4 Summary

To perform pH-dependent electrochemical experiments, a fully automated setup, the impedance titrator, was developed. With two different examples, the performance of the impedance titrator was shown. On the one hand, it could be shown that the introduced setup allows performing electrochemical experiments

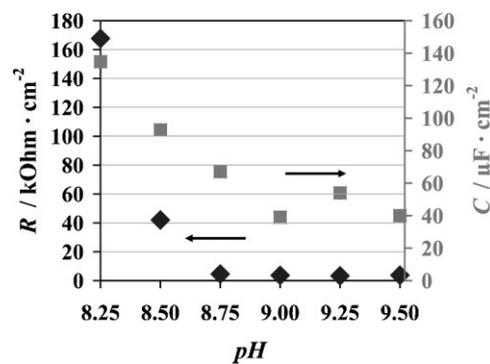


Figure 6. Resistance and capacity of an electrochemically grown alumina layer at various pH-values to determine the breakdown-pH of the layer

at a constant pH-value, using the active regulation mode. Even if hydroxide ions are consumed by a reaction, as described in Section 3.5, the pH-value is remarkably stable at $\text{pH} = 12.6$, ± 0.02 pH-units.

On the other hand, electrochemical experiments can be performed at defined, automatically set pH-values. In Section 3.6 the alkaline breakdown pH-value of an electrochemically grown alumina layer could be determined easily to a pH-value of 8.5, with an accuracy of 0.25 pH. The result complies with the theoretical value, calculated by Pourbaix [9]. Further applications could include an automatic determination of the inhibition performance of organic compounds such as carboxylic acid modified PEG [10] for Zn and carbonate or sorbate for Cu [11, 12].

5 References

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