Coupled Inductive Annealing-Electrochemical Setup for Controlled Preparation and Characterization of Alloy Crystal Surface Electrodes

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The present versatile multifunctional electrochemical crystal preparation-test station features capabilities for controlled thermal annealing of any type of (binary) metallic or oxidic catalyst or support crystal surfaces, in particular single crystals. The setup enables rapid inductive heating of the electrodes to temperatures up to 1900 °C under precise infrared temperature control in controlled gas atmospheres. The constant overpressure inside the cell prevents the ambient atmosphere to permeate and contaminate the process. Finely adjusted sensors afford accurate and instant information on the electrodes’ surface temperature. The subsequent cooling process in argon atmosphere proceeds without any treatment in water. After annealing, the crystals inside the chamber can immediately be subjected to any type of electrochemical deposition, modification, or characterization in two distinct three-electrode chambers, again without any exposure to air. Both chambers feature pump-controlled supply and withdrawal of liquid electrolyte. A special characteristic is the inert-gas flow inversion capability to transfer electrodes into separate portable inert-gas chambers. Design details are presented and their functionality during thermal preparation and electrochemical voltammetry of Ir(111) catalysts for the oxygen evolution reaction are demonstrated. The station provides a crystal handling environment superior to the classic flame annealing approaches, yet to constitute a cost-effective alternative to vacuum chambers.

Surface studies by means of single crystal electrodes have been widely researched since the early 40 s and are still extensively studied to establish model systems that can give insight into the rather complex behavior of poly crystalline materials.[1] The gained knowledge then can be employed to develop efficient, real-world electrocatalysts applied in energy conversion processes.[2] Single crystal electrodes need to possess an ordered and uniform surface structure free from impurities to be applied in electrochemical measurements.[3,4] A well-established technique to obtain well-ordered and clean single crystal surfaces is the use of Ar-ion bombardment and high-temperature annealing in high-priced ultrahigh vacuum (UHV) chambers in combination with surface science techniques.[5,6] While the atmospheric control is more sophisticated in UHV chambers than in the presented design, the former lack of accessible application. Their utilization and mainly the transport of electrodes between electrochemical cells and surface analysis section (low energy electron diffraction, X-ray photoelectron spectroscopy) are rather time consuming and complex. A more economical and sufficient approach employed for several decades is the flame annealing and quenching method.[7,8] Here, the cleaned electrode surface is quenched in milli-q water instantly after annealing and transported to the electrochemical cell.[9] However, the protection of the surface with a drop of water is limited to small electrodes with a diameter of <3 mm. Thus, it would be beneficial to combine the advantages of flame annealing[10] with subsequent electrochemical studies in a closed setup to ensure reproducibility and to prevent contamination of the surfaces. Furthermore, this would allow studying larger single crystals with an economical cell setup and would spread the availability of single crystal studies to more laboratories.

The modification of surfaces by underpotential deposition (UPD)[11–13] of (sub)monolayer amounts of foreign metal atoms opens the way to a variety of applications including the optimization of electronic structure of the active sites. This approach may be further extended to the preparation of surface alloys (SA) and near surface alloys (NSA) under controlled annealing conditions.[14–16] Besides the conventional approach in an UHV chamber, an inductive electrochemical single crystal chamber can give access to these surface modifications. In such a cell, the preparation and characterization of single crystal surfaces...
allows electrochemical surface design without exposing the electrodes to the laboratory environment.

A cell design meeting some of the challenges above was reported by Bondarenko et al.\cite{17} consisting of an inductive section and one three-electrode electrochemical section. We improved this initial design significantly by i) including a second electrochemical cell, ii) automated electrolyte dispensing and removal, iii) accurate automated infrared temperature control during inductive annealing, and iv) inert-gas flow conversion and crystal electrode transfer capabilities. Both electrochemical cells can be filled and emptied with electrolyte completely independently thanks to four separate purging electrolyte reservoirs. Here, we present this new test station for the first time and demonstrate their functionality using electrochemical measurements on Pt(111) and Ir(111) single crystals and a poly crystalline Ir\textsubscript{poly} electrode, evidencing the successful high-temperature annealing and surface modification. Any types of electrodes can be employed and heated by means of induction, as long as they exhibit sufficient critical mass and couple into the electric field. The wide accessible temperature range controlled by sensitive IR and the resulting precise control of the surface temperature is what sets this setup apart from all earlier designs. Given its cost effectiveness, this electrochemical test station is an affordable alternative to costly vacuum techniques and conventional flame annealing approaches.

In Figure 1, we introduce a detailed sketch of the custom-made inductive electrochemical single crystal cell with its two compartments. The electrochemical compartment at the bottom is equivalent to a typical three-electrode glass cell. The setup in our previous work\cite{18} was extended with a Luggin capillary at the bottom (see Figure 1) to enable clean and straightforward electrochemical measurements. With the use of two mass flow controllers (MFCs) the atmosphere inside the cell can be adjusted to N\textsubscript{2}, Ar, H\textsubscript{2}, CO, and any desired mixture thereof. The installation of a four-way valve at the gas inlet port atop the electrochemical section allows not only for the electrolyte to be degassed with
argon but also an air-free transport of the electrodes out of the cell. The transport of single crystal electrodes in the transfer chamber is described in detail in Figure 2a–e.

The preparation of reproducibly well-ordered noble metal single crystal surfaces is a fundamental basis for all electrochemical investigations on these facets. To this end, thermal treatment of a single crystal working electrode takes place in the second (inductive) compartment, until well-defined, atomically flat surfaces are obtained (confirmed by cyclic voltammetry, CV). Hereto, the working electrode can be positioned in the center of a quartz tube, which in turn is placed amid the inductive coil of an inductive heater (Desktop Induction Heater 30–80 kHz, 25 kW, EQ-SP-25A by MTI Corporation, USA). The lid of the inductive compartment is equipped with a gas outlet port. The cylinders are mounted with iridium wires, which are attached to four tungsten rods via iridium loops. The tungsten rods are placed in a glass tube, forming the working electrode mount, which is introduced to the cell via a GL (glass thread) fitting on the lid. A detailed description of the electrode mount is presented in Figure 3a–d.

An automatic heating system controller (OvenControl, lab-control, Berlin, Germany) is connected to two IR pyrometers (PyroUSB 2.2 series infrared sensor, Calex Electronics Limited) which need to be positioned manually prior to each heating protocol to accurately monitor the temperature of the crystal. Via a tactile contact, the inductive oven is automatically regulated through the temperature controller to a preset temperature and time. The heating protocol, defined by target temperature, holding time, and cooling phase, runs automatically and enables accurate and reproducible heating cycles. The combination of automated control, IR temperature measurement, and the iridium-tungsten electrode mount allows for annealing of single or polycrystalline electrodes at much higher temperatures than accessible through any direct contact thermocouple. Avoiding the direct contact also avoids any sintering between thermocouple and working electrode.

The smaller electrochemical cell, referred to as the “spoon” (see Figure 1c), is a small-scale three-electrode setup allows for additional “dirty” electrochemical measurements. A platinum wire runs through the spoon handle and ends at the ground of the spoon to serve as the counter electrode. A piece of platinum mesh is tack welded to the wire to guarantee a large enough surface area. An additional Luggin–Haber reference electrode capillary for measurements inside the spoon is mounted on a retractable inlet allowing access to measurements in the bottom compartment when not in use. Through the electrolyte inlet and outlet channels in the spoon handle, the electrolyte liquid in the spoon cell can be dosed and removed at will without contamination of the bottom electrochemical compartment and without exposure to ambient air atmosphere. A two-channel hydraulic pump controls the electrolyte flow automatically. The purposes of the spoon cell are not limited to electrochemical measurements, such as deposition of overlayers (OL) by UPD, but also to mechanically clean the electrodes with milli-q water. A novel and quite important feature of the overall test station is the continuing electrolyte stream through the spoon cell, which simplifies the cleaning process. Without removing the crystal electrode from the spoon cell, the milli-q water flow removes any adhering impurities prior to heat treatments as well as after each electrochemical measurement.

The presented novel test station setup is completed by four individual electrolyte reservoirs, which allow up to four different degassed electrolytes to be inserted into the electrochemical compartment at the bottom or into the spoon cell, thereby offering large flexibility to the user. These reservoirs are connected to the electrochemical compartment, the spoon, and the adjustable Luggin capillary via a pipe system. The electrolyte storage containers are constantly purged by Ar gas individually allowing for an air-free replacement of electrolytes between measurements.

The overall inductive electrochemical test station is further enhanced by a four-way valve to allow for a flow direction
inversion when the crystal electrodes are to be transferred to an external location like a synchrotron. Figure 2 displays the detailed procedure of the Ar-blanketed transfer of a crystal electrode to a portable glove box, inside which the electrode is placed under argon for additional transport. During annealing and electrochemical operation, the gas flow conditions are controlled as shown in Figure 2a. Gas flow direction from bottom to top serves to maintain a clean electrochemical compartment, as all removed impurities from the crystal surface leave the test station through the lid at the top into the waste. To ensure a safe transport, the electrodes are first pulled upward into the top part of the cell. Thereafter, the gas flow direction inside the station is inverted, then the top lid of the station is lifted and separated from the bottom of the station (see Figure 2b). The larger mass of Ar compared to air prevents the crystal electrode surface to come in contact with the ambient atmosphere. As shown in Figure 2c the lid is then positioned on top of a transport vessel, which is subsequently deaerated before both parts are attached to each other (Figure 2d). After flushing for several minutes more, both valves are closed and the lid of the cell can be separated from the Ar line.

The detailed steps involving the mounting of a single crystal electrode are presented in Figure 3. In order to increase stability and reliability, the mount is constructed of four tungsten rods (\( \varnothing = 1.60 \text{ mm} \)) which are rolled up at one end (i). The inside of the open O-shaped ends is coated with iridium (ii) to ensure electronic contact to the electrode. The cylinder is then suspended on four iridium hooks (iii) as shown step by step in Figure 3a–d.

In order to verify the full functionality of this new test station, a Pt(111) single crystal was inserted as working electrode for both the larger electrochemical bottom compartment and the spoon cell. Initially, the CV of the nonwell defined Pt(111) was recorded in the bottom electrochemical compartment without any previous annealing procedure in order to demonstrate the effect of surface structure healing during thermal preparation. As expected, the CV (shown as the dotted line in Figure 4a) displayed hardly any characteristic features of a well-ordered (111) facet of platinum except for a broad and undefined underpotentially deposited hydrogen (HUPD) region between 0.05 and 0.2 \( V_{\text{RHE}} \). A dramatic change in the cyclic voltammetry of the Pt(111) surface was observed after suitable thermal annealing at 800 °C for 2 min. Even after a short heating period, the spoon cell is fully sufficient to display characteristic electrochemical redox features of Pt and distinguish between chemically distinct adsorption sites. The voltammetry displays three typical regions of Pt(111): (i) the HUPD adsorption/desorption region at around 0.15 \( V_{\text{RHE}} \) with (ii) two shoulders at 0.25 and 0.3 \( V_{\text{RHE}} \) and (iii) a broad nondescript Pt oxidation region stretching from 0.85 to 1.2 \( V_{\text{RHE}} \).

The cyclic voltammogram of a single crystalline Ir(111) surface during preparation phase is presented in Figure 4b. The initial voltammetry of the crystal surface is largely featureless and only displays the hydrogen underpotential deposition (HUPD) and the exchange of sulfate and hydrogen sulfate from the electrolyte with adsorbed hydrogen atoms at potentials around 0.1 \( V_{\text{RHE}} \), respectively. With increasing number of heating cycles, the HUPD peak shifted to more negative potentials implying a more cathodic desorption of atomic hydrogen from the Ir(111) surface. The potential range between...
0.5 and 0.8 $V_{\text{RHE}}$ lacks any OH adsorption demonstrating a strong adsorption of sulfate and hydrogen sulfate, respectively.

Finally, in Figure 4c the catalytic activity with respect to the oxygen evolution reaction (OER) of a poly crystalline Ir electrode is compared to a bimetallic Ni/Ir$_{\text{poly}}$ surface with a monoatomic Ni OL and a bimetallic Ni/Ir$_{\text{poly}}$ alloy surface (NSA), all measured in 0.1 m KOH. Clearly visible is the electrochemical Ni(OH)$_2$/NiOOH redox transition in the CV of the OL at $\approx 1.4$ $V_{\text{RHE}}$ (see inset) proving that the conditions under which the UPD was conducted successfully forms a Ni overlayer on a polycrystalline Ir surface. Ni/Ir$_{\text{poly}}$ OL electrode additionally showed an increased OER activity when compared to pristine Ir$_{\text{poly}}$. When the Ni/Ir$_{\text{poly}}$ OL electrode surface was subsequently annealed at 400 °C for 2 min in a reducing atmosphere, the Ni atoms diffused into the Ir crystal and formed the near surface alloy structure (Ni/Ir$_{\text{poly}}$ NSA). [11,20] The formation of the surface alloy, likely with a single segregated Ir top layer, was evidenced by the absence of the Ni(OH)$_2$/NiOOH redox peak. This near surface alloy exhibited a slight loss in its catalytic OER activity when compared to the OL.

In conclusion, we demonstrate the successful design, assembly, verification, and utilization of a powerful coupled inductive annealing—electrochemical crystal electrode test station for preparation and characterization of well-defined and clean single crystal electrode surfaces in a controllable atmospheric environment. The rapid heating and temperature control up to 1900 °C in combination with a precise temperature protocol specification makes this cell unique among all previously reported electrochemical single crystal setups. In addition, the cell is well suitable for performing UPD measurements in a spoon-like three-electrode setup with subsequent annealing for appropriate alteration of surface properties and reactivities.

**Experimental Section**

Before the single crystal electrodes were mounted into the setup, the glassware was cleaned thoroughly in a solution of 95% H$_2$SO$_4$ and an oxidizer (NOCHROMIX, Sigma-Aldrich), followed by a bath in 0.1 m HNO$_3$ and repeated rinsing with milli-q water. The spoon cell, however, was rinsed with 37% HCl due to the integrated Pt wire.

Two types of verification measurements were applied to test the cell. In a first step, electrochemical measurements of a Pt(111) single crystal surface were performed in both electrochemical compartments to confirm the principle operation of the cell setup. Afterward, the second verification measurement proves the application to higher annealing temperatures by preparation of an Ir(111) single crystal as well as UPD and (near-) surface alloy formation by annealing a polycrystalline iridium electrode.

For the first experiment, a Pt(111) single crystal electrode with a diameter of 10 mm and a precision of orientation of $\leq 0.1$° (MaTecK GmbH, Jülich) was used. For mounting, two continuous lateral holes with a diameter of 0.5 mm were machined into the shell surface through which loops made of Ir wire (Alfa Aesar, $\varnothing = 0.25$ mm, 99.9%) run. A saturated mercury/mercury sulfate reference electrode was applied and calibrated frequently against a reversible hydrogen electrode (RHE) in the same electrolyte at room temperature. Before the Pt(111) single crystal was heated in the inductive compartment, a cyclic voltammogram of its surface was recorded in the bottom compartment. After annealing at 800 °C in Ar atmosphere (purity 5N, 99.999%) for 2 min, the surface of the electrode was characterized in the spoon cell.
In experiment 2, the single crystalline iridium measurements were done as described in ref. [18]. These verification measurements were performed in 0.05 M H₂SO₄ (diluted from 95% H₂SO₄ Suprapure, Carl Roth). Ir(111) electrodes with a diameter of 10 mm and a precision of ≤0.1° (MaTeck GmbH, Jülich) were used.

For evaluation of the surface quality, the electrodes were immersed in the hanging meniscus configuration into the argon degassed electrolyte at the lower potential limit of 0.05 V_RHE. A cyclic voltammogram at a scan rate of 50 mV s⁻¹ was then recorded. The upper turning potential for Pt was 1.2 V_RHE and 0.8 V_RHE for Ir.

The UPD measurements were conducted with a poly crystalline Ir electrode (Ø = 10 mm, MaTeck GmbH, Jülich) grinded and polished in a half automatic polishing machine (AutoMet 250, Buehler) to a mirror-like surface finish. The deposition measurement to obtain an OL of Ni (Ni/Ir_poly, OL) was performed in phosphate buffer solution (0.1 M KH₂PO₄, 0.1 M K₂HPO₄ containing 2 × 10⁻³ M NiSO₄. The electrode was immersed at the deposition potential 0.05 V_RHE and held for 10 min. To produce a Ni/Ir_poly NSA the electrode was subsequently annealed in 4% H₂/Ar at 400 °C for 2 min. Both catalysts were then tested for OER activity in 0.1 M KOH after thorough rinsing with milli-q water. The samples were immersed in the hanging meniscus configuration at 1.0 V_RHE followed by a polarization curve into the OER potential region with 5 mV s⁻¹ to an upper potential limit required to reach a current of 0.785 mA (current density of 1 mA cm⁻²) in the respective scan.

The measured current is normalized to the geometric area of the electrodes to provide comparable current densities (j_geo). The geometric surface area of the electrodes is 0.785 cm² corresponding to the diameter of 10 mm.

The electrolytes in the reservoirs were degassed with Ar for 15 min before they were introduced into the cell.

All electrochemical measurements were performed by using a potentiostat (SP-240, BioLogic, France).

Keywords
inductive electrochemical cell, iridium, single crystals, surface alloys, water splitting

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Conflict of Interest
The authors declare no conflict of interest.