Active Temperature Control in Photoelectrochemical Measurements - Metrology for Artificial Photosynthesis

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Abstract

The temperature has a large impact on the rate of a chemical reaction. For photoelectrochemical water splitting it has been shown that the photocurrent of a tungsten oxide anode increases by 64 % in a temperature interval of 25 to 65 °C.

Photoelectrochemical cells are usually not equipped with systems for active temperature control. This limits the reliability of measurement data, especially for long measurements under illumination (e.g., impedance spectroscopy). Insufficient comparability of materials is an obstacle for development and application of photoelectrochemical modules.

Active Temperature Control in Photoelectrochemical Measurements

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Metrology for Artificial Photosynthesis

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Objectives

- **Integration of temperature control** in a metrological test setup for photoelectrochemical water splitting
- **Investigation** of the temperature effect on different (photo)electrochemical systems

Experimental approach

- Commercial **PEC cell** (Zahner) without possibility for heat transfer by double jacket or heating elements
- **Peristaltic pump** for circulation of corrosive electrolytes through a closed system of silicon tubes
- Voltage-controlled **Peltier element** with aluminium heat sink in close contact with the silicon tubes
- Electronic **temperature sensor**, situated between PEC cell and Peltier element (without electronic feedback loop)

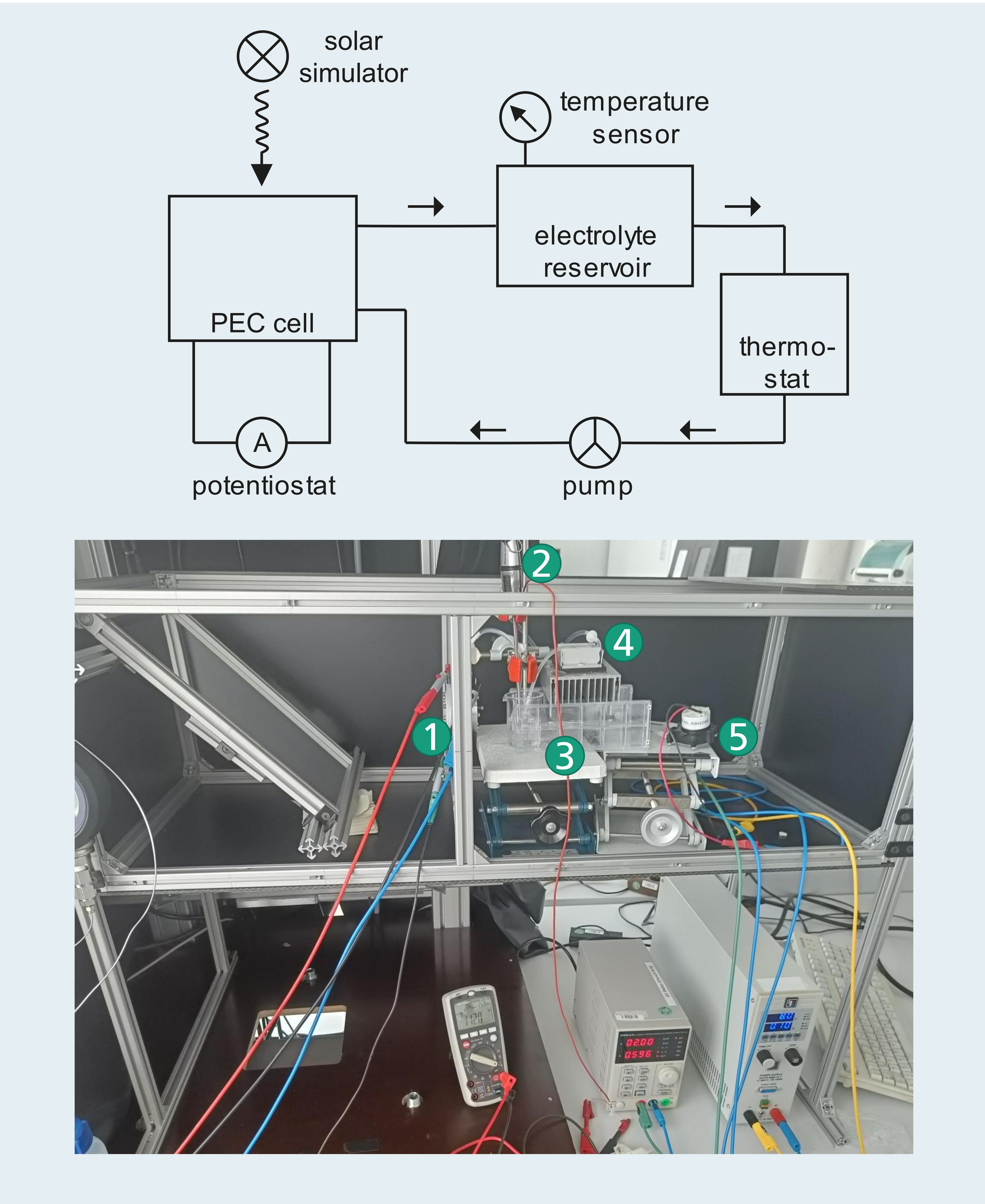

Figure 1 Scheme of the experimental setup and photograph (1 PEC cell, 2 temperature sensor, 3 electrolyte reservoir, 4 Peltier element, 5 peristaltic pump (potentiostat and solar simulator not visible)

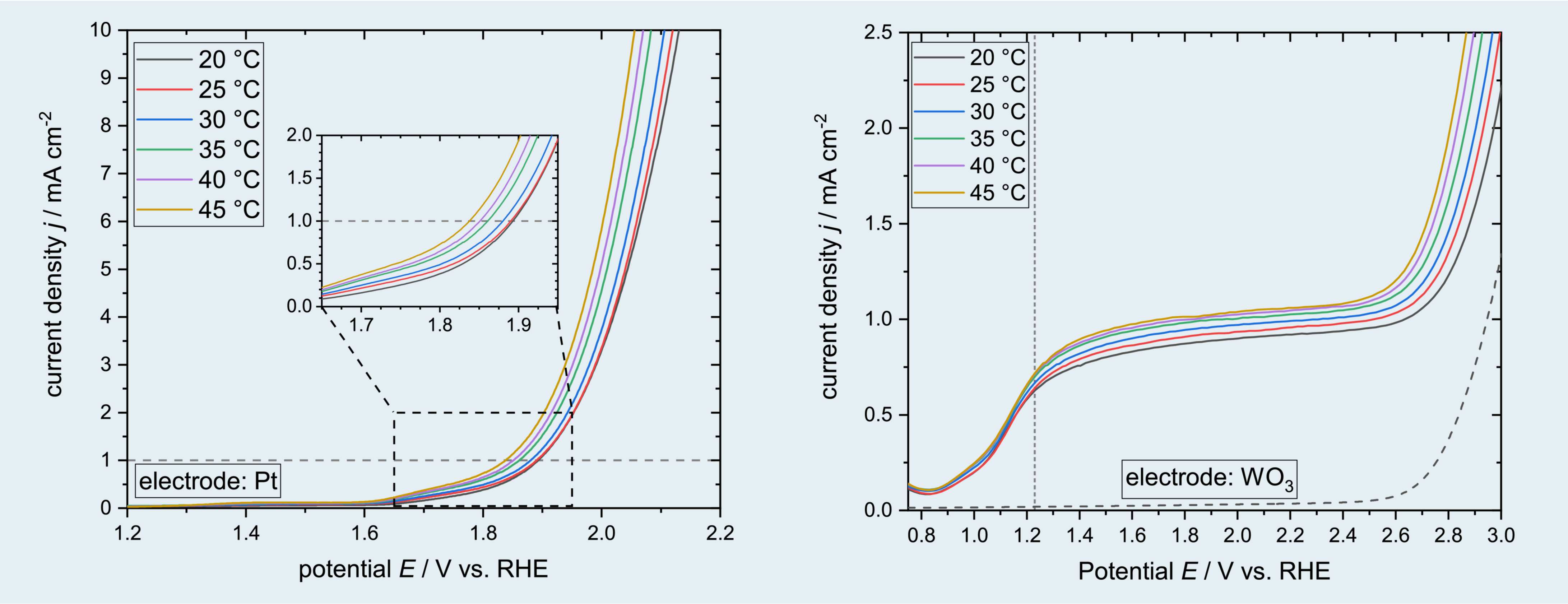

Figure 2 Photocurrent density vs. potential using two platinum electrodes (left) or a tungsten oxide photoanode and a platinum cathode (right) at temperatures changing by 5 K between 20 °C and 45 °C. The left plot is measured without illumination, the right with illumination (100 mW cm^{-2}, AM1.5G).

Results

The temperature control unit allows measurements in a **temperature range of 20–45 °C** (at room temperaturs of 25–30 °C). **Thermal stability of ±1 °C** is achieved over the range of hours. The circulation induces minor noise in the measurement data (approx. 1 µA), which can be eliminated by statistical methods (*e.g.*, moving average).

Two different systems were studied to test the setup and to investigate the influence of the temperature on the reaction:

1. As proof-of-concept, two **platinum electrodes** were used to perform electrolysis of an acidic electrolyte. The temperature effect is widely known for this system and there are no overlaying effects. Linear scanning voltammograms (Figure 2, left) show a significant influence of the reaction temperature on the current. The overpotential (measured at 10 mA cm^{-2}) decreases by more than 50 mV in a temperature interval of 20–45 °C. The effect is a result of changing thermodynamic parameters (*e.g.*, temperature dependence of $E_{H2O/O2}$) and kinetic factors (*e.g.*, ion transport).
2. A sputtered, nanostructured **tungsten oxide photoanode** was investigated to show the effect on photoelectrochemical systems. The measurements were complicated by unwanted time-depended effects (*e.g.*, reaction kinetics, corrosion). After optimization of measurement parameters a correlation of photocurrent and temperature was found. The saturation photocurrent density increased by 15 % for a temperature rise of 25 K (20–45 °C), which is close to the published values.[1] The onset potential of 0.8 V_{RHE} does not depend on the temperature. The onset of the electrolysis reaction was affected similar to the investigated Pt electrodes.

Benefits

- **Higher quality of measurement data** (*e.g.*, impedance data of illuminated sampes) by active temperature control
- **Increased reproducibility and comparability** of measurements
- **Additional data** for simulation of electrode performance under real-world conditions

Conclusion

The developed system for temperature control allows to investigate the temperature dependency of photoelectrochemical water splitting and enables measurement routines with high metrological precision.

Literature

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[2] S. Cao, L. Piao, *Angew. Chem. Int. Ed.* **2020**, *59*, 18312–18320.

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