A measurement system for photoelectrochemical processes with high quality irradiation, temperature control and automated gas analysis

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Abstract

In this Application Note, a versatile and reliable measurement system for photoelectrochemical investigations is described which aims to assist scientists in obtaining reproducible photoelectrochemical data of high quality, including the solar-to-hydrogen (STH) efficiency. Specifically, it addresses the parameters irradiation quality, reaction temperature and gas measurement. The setup is designed to exclude stray light and uses a solar-grade mirror to reflect the light of a vertical solar simulator on the electrochemical cell. The light quality in the setup (≫AAA≪, IEC 60904-9) is close to the classification of the solar simulator itself. The temperature in the electrochemical cell is controlled with an external Peltier element and can be kept constant in the range of 20–45 °C. The influence of reaction temperature on the photocurrent of a WO_3 photoanode is demonstrated. The gaseous reaction products are analyzed with a mobile gas chromatograph, using an automated measurement routine with discontinuous sampling from the electrochemical cell. The system is applied to determine the Faraday and STH efficiencies of a copper indium gallium selenide photocathode.

Introduction

Hydrogen is seen as a key element of a future carbon-free economy. The International Energy Agency forecasts that the hydrogen demand will increase from 90 Mt (2020) to 260 Mt by 2050 if the currently existing government programs are implemented.[1] Yousif *et al* . calculated a demand of 568 Mt for a scenario which meets the goals of the Paris Agreement (2015). [2]

Currently, hydrogen is produced primarily from fossil resources (*e.g* ., steam reforming, coal gasification). Carbon neutral production is possible through water electrolysis with electricity from renewable resources, which is expected to play a major role in the coming years even through its present contribution to the global hydrogen production is negligible.[1] However, scaling-up electrolysis will require an corresponding expansion of the energy infrastructure, which adds to the investment costs. For example, an expansion of the power grid will be necessary in central Europe, because wind and solar plants are placed decentral and are spatially separated from large-scale electrolyzers. A solution to this problem could come from approaches which combine energy uptake and hydrogen production in a single system (≫artificial photosynthesis≪) and offer a cost-effective alternative for low production volumes and off-grid applications.[3]

Photoelectrochemical (PEC) water splitting is a method of artificial photosynthesis, in which illuminated semiconductors (*e.g.* , WO_3, Fe_2O_3) in direct contact with an aqueous electrolyte cause the splitting of water molecules to hydrogen and oxygen without the need for traditional photovoltaics or electrolyzers. Selected systems achieve high efficiencies of up to 19%, and a photoelectrochemical solar park with an active area of 100 m^2 was constructed and operated for several months.[4, 5] However, semiconductors that offer a balanced

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set of properties (efficiency, stability, cost and scalability) are lacking.[6] Therefore, large parts of the current research still focuses on material development on the laboratory scale. Among the common measurements are methods for electrode characterization (e.g., voltammetry, stability measurements, impedance spectroscopy), and methods for determining device metrics (e.g. the solar-to-hydrogen efficiency, STH).[7]

It has been pointed out that measurements on similar materials in different labs lead to different results, which was attributed to a lack of accepted standards.[8] A number of recent reviews addresses this issue, provides guidelines for measurement routines and gives best-practice examples, e.g. for the solar-to-hydrogen (STH) efficiency.[7,8,9,10] A second reason for insufficient comparability is that photoelectrochemical measurements require special equipment that is not common in chemical laboratories and is challenging to install and operate (e.g., solar simulators, gas chromatographs). It has been shown that standard measurement routines are prone to systematic errors induced by the equipment (*e.g*., solar simulators), which can result in an overestimation of the efficiency.[11]

In this Application Note, we present a versatile and reliable measurement system for PEC water splitting which allows to obtain high quality electrochemical data, including the STH efficiency. It addresses three major issues which, to our experience, pose difficulties in many labs and can hamper the accuracy and reproducibility of measurement data: (1) the implementation of large area light sources with high spectral quality, (2) the stabilization of the reaction temperature under irradiation, and (3) the quantitative determination of hydrogen.

Materials and methods

Materials: Experiments were carried out with a photoanode of sputtered WO_3 on fluorine doped tin oxide (FTO) (WO_3/FTO/glass, $d_{WO3} = 1$ µm) or with a sputtered $Cu(Ga,Se)(S,Se)_2$ (CIGS) photocathode (CIGS/Mo/glass, $d_{CIGS} = 0.25$ µm). 1.0 M $HClO_4$ and 0.1 M H_2SO_4 were used as electrolytes and were purchased from Carl Roth (Rotipuran p.a.).

Methods: Illumination (spectrum AM1.5G) was provided by A+AA LED solar simulator (SINUS 270, Wavelabs). Intensity calibration to 100 mW cm^{-2} was carried out with a monocrystalline Si reference solar cell (ReRa Solutions). The spectral distribution was measured with a Zeiss MCS UV-NIR spectrometer. The spatial non-uniformity was determined with a Homogeneity Tester (Fraunhofer CSP). The temporal stability was recorded with a Si reference solar cell.

The system for temperature control was constructed with a 65 W Peltier element with two heat sinks, a 12 V peristaltic pump (Grothen), silicon tubes ($d = 3$ mm) and an electrolyte reservoir of 20 ml.

Gas measurements were carried out with a »Mobile GC2« (ECH Elektrochemie Halle), which was optimized by the manufacturer for the measurement of H_2 and O_2 in photoelectrochemical water splitting experiments. A sampling and analysis loop was implemented that enables automated acquisition and evaluation of the Faraday and STH efficiency.

Photoelectrochemical measurements were carried out in a commercial PEC cell (PECC2, Zahner Elektrik). The working electrode had a fixed diameter of 1.8 cm ($A = 2.54$ cm^2). An Ag|AgCl electrode was used as reference electrode and a coiled platinum wire as counter electrode. The Faraday and the solar to hydrogen efficiencies were measured in a Porto cell [12] with a platinum mesh as counter electrode. Bias was provided by a photovoltaic module (5 cSi cells in series, $A = 6.0$ cm^2), mounted parallel to the absorber.

Current-voltage curves were recorded in the dark or under constant illumination at a scan rate of 100 mV s^{-1} between 0.6 V_{RHE} and 2.7 V_{RHE} with a maximum current of 5 mA. Before each measurement, the samples were equilibrated at 0.6 V_{RHE} for 60 s. The potentials versus the reversible hydrogen electrode (RHE) were calculated by

$$E_{RHE} = E_{AgAgCl} + E^0_{AgAgCl} + 0.059 \text{ x pH}$$

with $E^0_{AgAgCl} = 0.209$ V. Onset potentials were determined as intercept of a tangent with the abscissa.

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Results and discussion

The PEC measurement system (Figure 1) has been designed to work with a standard vertical solar simulator. It offers room for PEC cells with absorber sizes of up to 16x16 cm2, as well as for the required equipment (e.g., for temperature control),

The system is built from a metal frame and six cardboard plates and houses a solar-grade mirror and a sliding holder for the electrochemical cell. The frame is made from commercial aluminum profiles and has feet which are separately height-adjustable to allow installation on tables or over edges. Five fixed and one removable cardboard plates are attached to the frame. Black surfaces on the inside prevent light reflection, which could otherwise result in an increased irradiation on the photoelectrode. With a closed front side, the setup protects the experimenter from irradiation. The light of a vertical solar simulator enters the setup from above and is reflected by a tiltable solar-grade mirror on the PEC cell. A sliding cell holder supports the positioning of the cell with a high degree of reproducibility. It fixates the cell on the platform and minimizes the danger of spilling chemicals. The holder can be removed if large cells are investigated. The system can be equipped with different PEC reactor types, a potentiostat and auxiliar equipment for monitoring, imaging, or spectroscopic applications.

Table 1 Geometrical data of the PEC measurement system with data for spatial non-uniformity according to IEC 60904-9

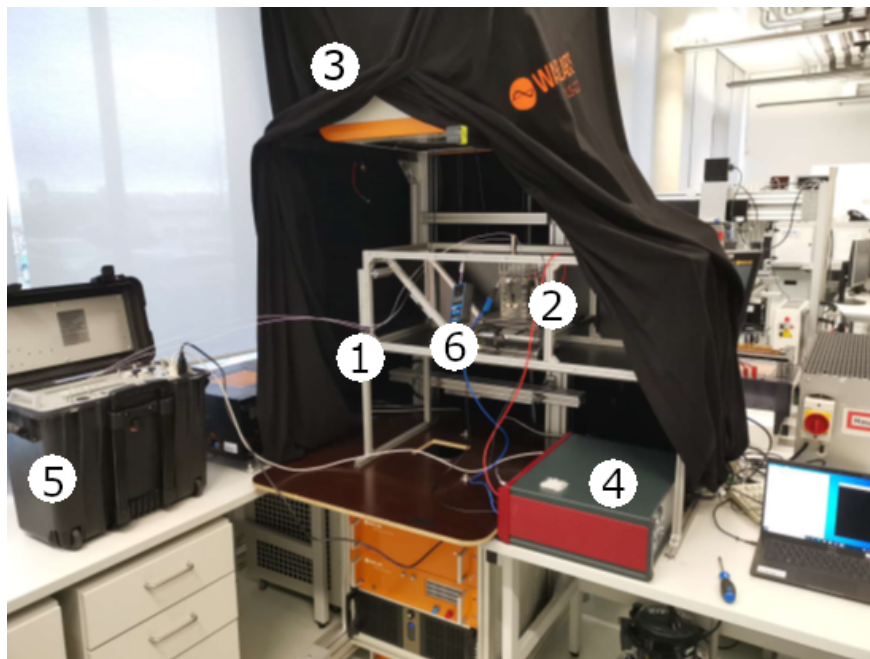| Platform dimensions (WHD)	100 x 40 x 30 cm^3
Mirror dimensions	20 x 30 cm^2
Light field (class A)	10 x 10 cm^2
Light field (class B)	12 x 12 cm^2
Light field (class C)	16 x 16 cm^2

Figure 1 Photograph of the measurement system with equipment for gas measurement (1 measurement system, 2 electrochemical cell, 3 solar simulator, 4 potentiostat, 5 gas chromatograph, 6 pressure sensor)

Characterization and classification of irradiation

Light accounts for the main part of the energy input in photoelectrochemical measurements. It is common for photoelectrochemical experiments to use the global standard spectrum AM1.5G (IEC 60904-3) and to calibrate its intensity to 100 mW cm^{-2} with a reference solar cell. The quality of a solar simulator is defined in IEC 60904-9 by three parameters which are spectral match, spatial non-uniformity and temporal instability. Since the test setup contains a mirror which possibly affects the irradiation quality, the parameters were determined and compared with the characteristics of the solar simulator.

The spectral distribution was measured with a spectroradiometer on four points in the plane of the photo-electrode. The classification is based on the cumulative intensity in six spectral ranges between 300 and 1200 nm. The measurements found that the deviation is maximal in the predefined spectral range of 772–919 nm, where it is 14.8 %. This resulting classification of »A« is lower than the classification of the solar simulator (»A+«), which is probably due to a spectral dependence of reflection of the mirror.

The spatial non-uniformity of the light is especially important for the investigation of large photoelectrodes. It was be measured with an array of intensity-calibrated cSi solar cells. The classification is based on the ratio of the largest and smallest irradiance according to $(I_{max}-I_{min})/(I_{max}+I_{min})$. Depending on the investigated area, classifications of »A«, »B« and »C« are obtained in the investigated setup (Table 1). The degrading uniformity on larger areas is a result of the limited mirror size.

Temporal instability of irradiance is defined by short term and the long instability, of which only the latter is relevant for PEC measurements. It can be determined from the light intensities before and after a PEC experiment by $(I_{max}-I_{min})/(I_{max}+I_{min})$. A value of below 0.02 was found in the investigated setup, which allows a classification of »A«.

It has to be noted that the use of Si solar cells for the measurement light intensity, spatial non-uniformity and temporal instability is legitimate only for absorbers with a similar band gap.[11] Since many semiconductors for water splitting experiments have higher band gaps (*e.g* ., WO$_3$, 2.8 eV) an uncertainty is induced which will be especially prominent when solar simulators with poor spectral fit are used.

Stabilization of the reaction temperature

The rate k of a chemical reaction depends on the reaction temperature. For many chemical reactions an exponential relationship of $k = A \exp[-E_A/(RT)]$ is found, whereas the processes within the semiconductor usually result in a negative temperature coefficient. For the example of WO$_3$ photoanodes it was measured that the photocurrent increases by 64 % in a temperature interval of 25 to 65 °C.[13]

Commercial photoelectrochemical cells are usually not equipped with systems for temperature control (*e.g* ., double jackets). We found that the temperature in an idle cell under illumination with an LED solar simulator rises by 3 °C in 10 min. For Xe arc lamp-based systems the temperature increase is probably higher due to their stronger IR emission. The changing temperature can limit the reliability of measurement data, especially for long measurements under illumination (*e.g* ., voltammetry, impedance spectroscopy).

In the developed system (Figure 2) for temperature control, the PEC cell is connected to a closed loop of silicone tubes. A peristaltic pump, which allows the use of acidic or alkaline electrolytes without corrosion, circulates the electrolyte with a flow rate of 60 ml min^{-1}. Heat exchange occurs through the silicon tubes which are wound through the fins of an aluminum heat sink on a voltage-controlled Peltier element. The temperature is measured with an electronic sensor in an electrolyte reservoir situated between the cell and the Peltier element. An automatic control of the Peltier element with the sensor data is possible but has not yet been realized.
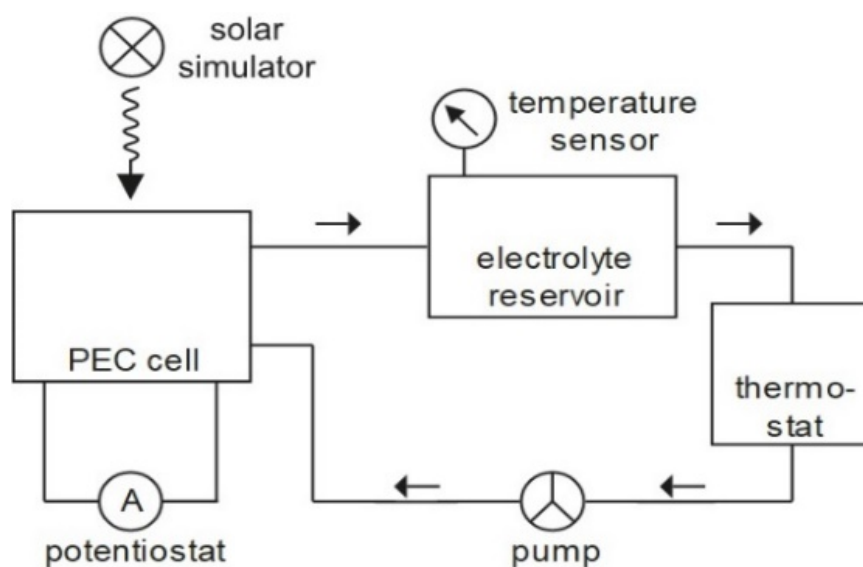
Figure 2 Block diagram of the system for temperature control

The system allows to carry out measurements at stable temperatures (± 1 °C) in the range of 20–45 °C (measured at room temperatures of 25–28 °C). The circulation induced minor noise in the measurement data (approx. 1 µA), which could be eliminated by statistical methods (*e.g* ., a moving average).

The effect of the temperature on the reaction was investigated on the example of a sputtered WO_3 photoanode (Figure 3). While the onset potential under illumination is independent of temperature in the investigated interval, the onset potential of the dark reaction decreases slightly (Table 2). The photocurrent density increases by approximately 15 %, both at 1.23 V_{RHE} and in the plateau region. The results are close to published values.[13]

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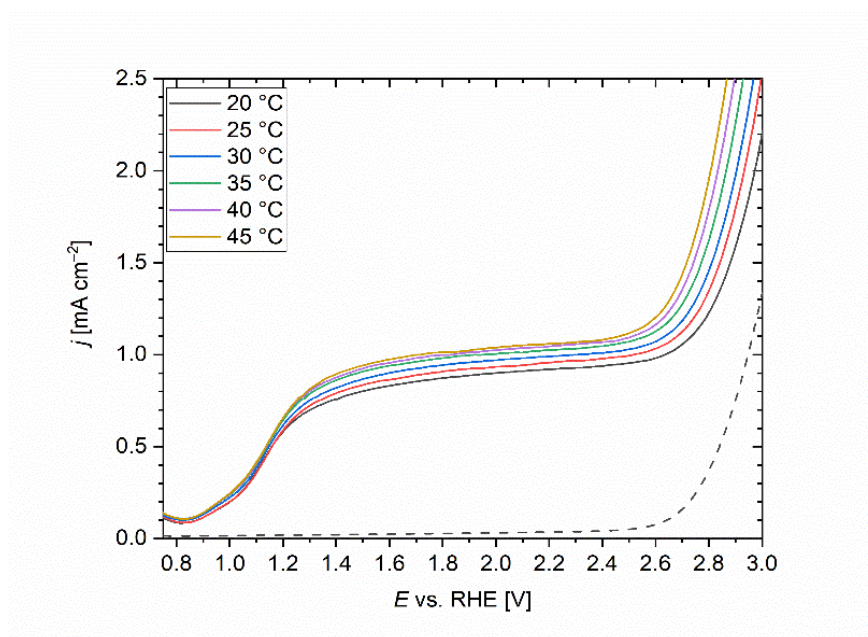
Figure 3 Temperature dependent photocurrent density of a WO$_3$ photoanode (linear sweep voltammetry, solid lines illuminated, dashed line not illuminated)

Table 2 Results from linear sweep voltammetry at 20 °C and 45 °C

	20 °C	45 °C
E_{onset} (light)	0.85 V$_{\text{RHE}}$	0.85 V$_{\text{RHE}}$
E_{onset} (dark)	2.81 V$_{\text{RHE}}$	2.69 V$_{\text{RHE}}$
j (1.23 V$_{\text{RHE}}$) [µA cm^{-2}]	626	719
j (2.00 V$_{\text{RHE}}$) [µA cm^{-2}]	913	1060

The data allows to estimate the error of a measurement without temperature control: During a measurement time of 10 min the temperature increases by 3 °C, which results in an error of 2.6 % results in the photocurrent. This could be acceptable for standard material screening but should be avoided in high-quality measurements. It has to be noted that the temperature effect can be different for other systems.

Automated GC measurement routine for STH determination

The desired product of an electrochemical reaction is measured quantitatively for the determination of the Faraday efficiency, which is an important parameter of an electrode/electrolyte combination. Side reactions (*e.g* ., with the electrolyte) or subsequent reactions (*e.g* ., with cell components) result in a Faraday efficiency below 100 %. In photoelectrochemical water splitting, quantitative determination of hydrogen and oxygen has been carried out with mass spectrometers [14] or with electrochemical sensors [15], but the most common way is to measure with gas chromatographs. The integration of gas chromatographs is a demanding task, as leakage can be a serious problem. The accuracy is often limited by low gas amounts and by the accuracy of supporting measuring devices (*e.g.* , volume flow controllers).

The presented test setup aims to mitigate these problems by the use of a commercial mobile GC which was optimized by the manufacturer for PEC applications. The TC is equipped with an integrated Ar tank, a thermal conductivity detector and two short columns to allow fast measurements. It is connected to a Porto cell via metal gas transfer lines with standard metric threads. A pressure sensor and a safety valve are connected as well (Figure 4).
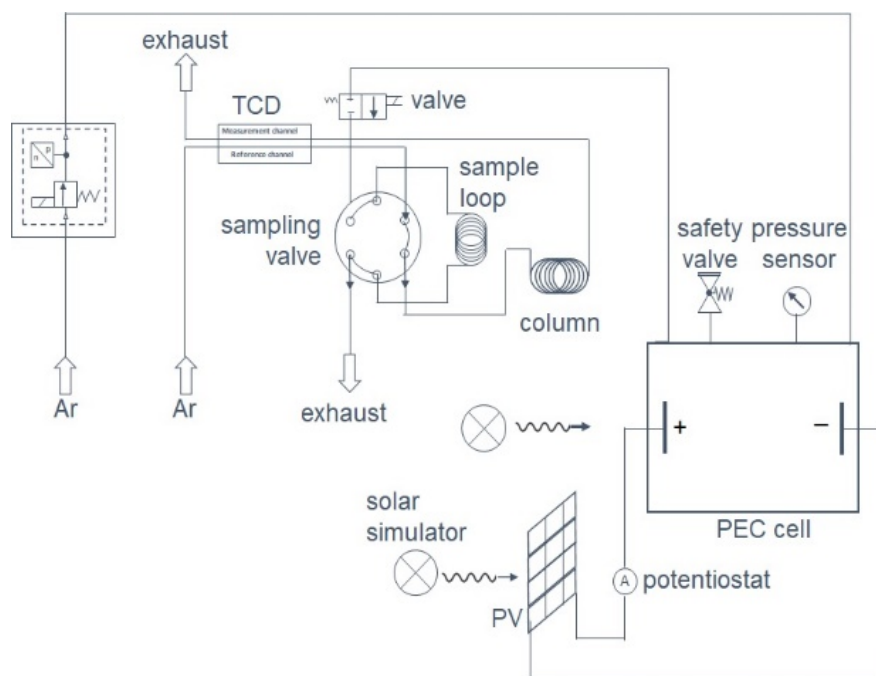
Figure 4 Block diagram of the system for gas measurement

The analysis is carried out by an automatic measurement routine. The time-resolved data is sequentially acquired in series of cycles, each of which consists of three steps (Figure 5):

The pressure in the electrochemical cell is set to 1.1 bar with Ar from the integrated tank of the GC. In this step, the hydrogen concentration drops.

With all valves closed, the water splitting reaction is started by switching on the solar simulator. The episode may last for 300 s but can be expanded if photoelectrodes with low efficiencies are investigated. Pressure and hydrogen concentration in the cell increase linearly.

3. A valve in the GC is opened and allows the gas mixture in the electrochemical cell to relax through the sampling valve. After a certain volume flow, which correlates with the volume of the metal tubes, the sample is taken. The GC measurement is started and runs parallel to steps 1 and 2.

After the automatism is terminated by the user, the data of the GC, the pressure sensor and the potentiostat are loaded into an Excel® script which calculates the molar amounts of hydrogen and oxygen, the Faraday efficiencies and, if applicable, the STH efficiency. Leakage is detected by a continuous pressure drop in the cell during an idle period and can be corrected to a limited extend.
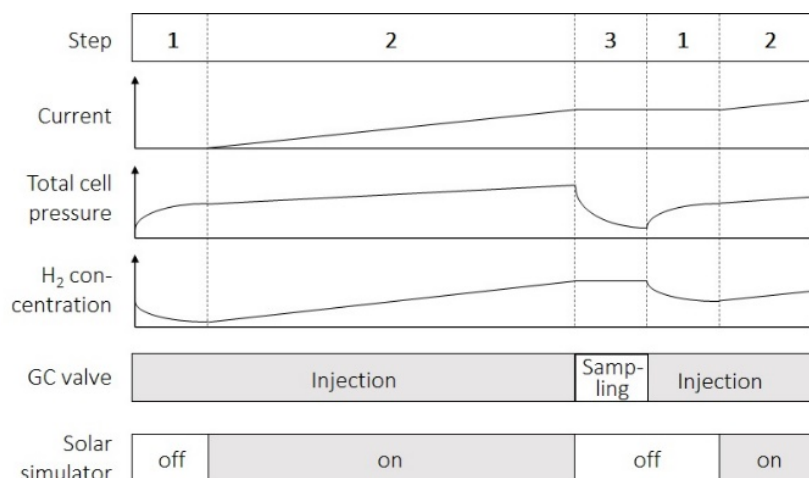
FIGURE 5 Procedure of the automatic measurement routine with schematic data for current, cell pressure and H_2 concentration.

The system was applied to investigate a photocathode of copper indium gallium selenide in H_2SO_4, for which a Faradaic efficiency of (95.4 ± 7.7) % was determined (Figure 6). The STH efficiency was calculated to be (1.9 ± 0.1) % for a system of a 25.0 cm^2 photocathode and a 6.0 cm^{2}photovoltaic module. Both efficiencies agree with previous literature values [16].

A quantitative error analysis with consideration of the propagation of uncertainty shows that the free gas volume of the electrochemical cell is an important contribution to the overall error, for which an individual measurement uncertainty of 2 mm^3 results in an absolute error of 0.9 % in the Faraday efficiency. The determination of the absorber area, variations in the reaction temperature and non-ideal behavior of the gas/liquid system (*e.g.* , trapped gas bubbles) are significant contributions to the error. The GC measurement itself has a high accuracy with an error of less than 0.01 % but relies on the quality of the calibration.
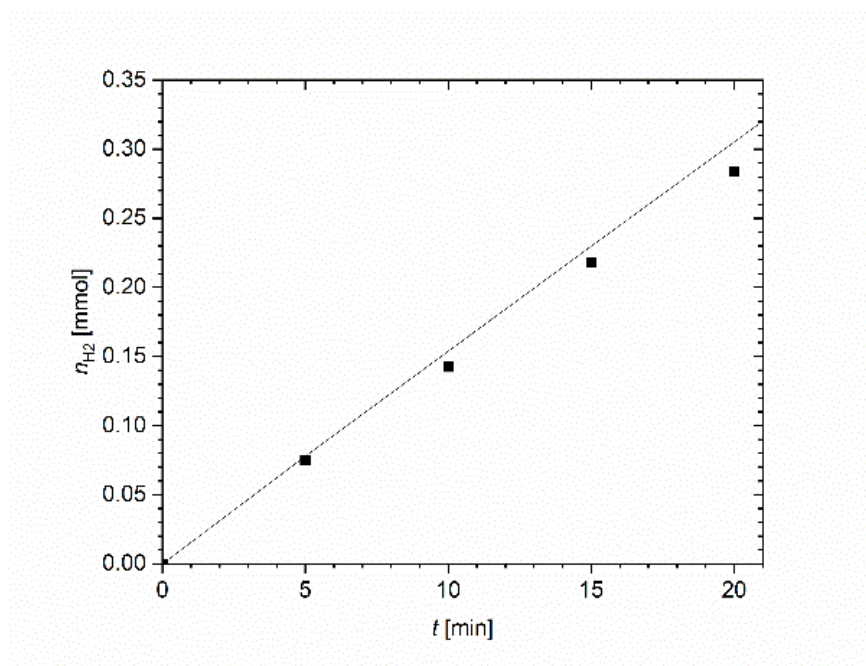

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Figure 6 Measured vs. calculated molar amounts of H$_2$ for a CIGS photocathode

Conclusion

The test setup allows to conduct various photoelectrochemical measurements (e.g., STH determination) and can help to avoid common problems with equipment. It allows the use of standard vertical solar simulators by reflecting the light to the electrochemical cell with a solar-grade mirror. The light in the plane of the photoelectrode had a high spectral quality, a low spatial non-uniformity and a low temporal instability, resulting in an AAA classification (IEC 60904-9). A system for temperature control with an external Peltier element allows measurements at constant temperature ($\pm$1 °C) in the range of 20–45 °C. It enables automated time resolved measurements with enhanced metrological precision and the investigation of the temperature dependency of photoelectrochemical reactions. Gas analysis is carried out with a mobile GC, which is equipped with a thermal conductivity sensor, two short columns and an internal gas supply. It makes use of an automated measurement routine with discontinuous sampling from the reactor cell. A software for data evaluation calculates Faraday and STH efficiencies and allows the correction of leakage. The system was applied to investigate a copper indium gallium selenide photocathode in H$_2$SO$_4$, for which a Faradaic efficiency of (95.4$\pm$7.7) % was determined.

Conflict of Interest Statement

The authors declare no competing interests.

Data Availability Statement

CAD models, the software for GC data evaluation and data that support the findings of this study are available from the corresponding author upon reasonable request.

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