S1:

To show the repeatability and stability of the setup, another experiment has been conducted, in which a new cathode and fresh electrolyte have been used. After an initial run-in phase of about 2 hours, that is not shown in this Fig. S1, the current yield approaches 1.0, showing the excellent predictability of the hydrogen output of the system.

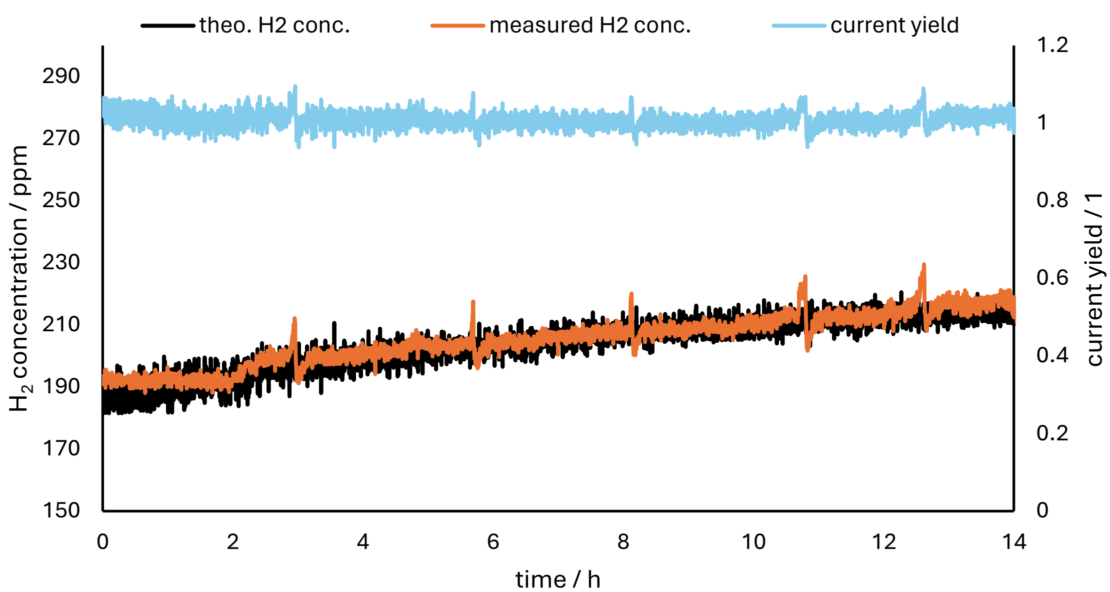

Figure S1: Diagram of a long-term experiment that was set up with a new cathode and new electrolyte. Although the current slowly increases over the duration of the experiment, the current yield stays consistently at 1.0 showing that the expected output (by measuring the electric current flowing through the cell) exactly matches the measured output.

The amount of hydrogen increases over the duration of the experiment. However, this drift has no influence on the predictability of the system itself, as the electric current increases in the same proportion as the measured (real) hydrogen concentration. Therefore, the current yield remains at ~1 and the hydrogen output stays absolutely predictable by measuring the electric current and applying Faraday´s law of electrolysis. The reason, why the electric current increases might be explained by an increasing surface roughness (and therefore a larger surface area which leads to a lower electric resistance of the electrolysis cell), or voltage drifting of our (low cost) power supply.

The “peaks” that are visible in Fig. S1 are likely due to changes in relative humidity. Out of question are influences by other experiments, or people residing in the lab, as the experiment was conducted over night. From our experience, we can say that electrochemical sensors are sensitive to humidity changes and a sudden change (as might be caused by switching of the air conditioning in the lab) causes the sensor to behave in the way as is happening in the experiment series shown in Fig. S1. As the sensor adjusts in a matter of 10 to 20 minutes to the new humidity, this behaviour has no influence on the results itself.

S2:

Accuracy of the standard obtained & Faraday´s first law of electrolysis:

The accuracy of the standard that is obtained is directly proportional to the current yield of the reaction, that is shown in the diagrams. A current yield of 1.00 means that the measured concentration is the same concentration as is predicted by applying Faraday´s first law of electrolysis and incorporating the dilution with ambient air (500 mL/min in our experiments). The current yield η_c calculates according to the following formula:

$$\eta_c = \frac{c_{\text{measured}}}{c_{\text{theoretical}}}$$

A current yield of 1.00 therefore results in a totally accurate standard.

The theoretical amount of hydrogen *n* produced in a certain amount of time *t* can in turn be calculated with Faraday´s first law of electrolysis with the electric current *I*, the number of electrons used in the reaction *z* and the Faraday constant *F*.

$$n_{\text{Product}} = \frac{It}{zF}$$

The theoretical amount of hydrogen that is produced per minute, combined with the dilution flowrate gives the theoretical concentration of the resulting gas mixture. This theoretical concentration is then compared to the actual measured concentration to obtain the current yield of the system.