**Supporting Information for:**

Silver Leakage from Ag/AgCl Reference Electrodes as a Potential Cause of Interference in the Electrocatalytic Hydrogen Evolution Reaction

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**SI-1: General Experimental Remarks:** Sulfuric acid (95%) was purchased from Fisher. 0.180 mm-thick Nafion N-118 membrane, carbon graphite sheet (0.25mm diameter), boric acid 99.99%, Amberlite® IRC-748 and phosphoric acid (85%) were supplied by Alfa Aesar. Potassium hydroxide (90%), perchloric acid, sodium hydroxide (98-100.5%) and sodium phosphate dibasic (98.5%) were purchased from Sigma Aldrich. All chemical reagents were used as purchased.All electrolyte solutions were prepared with reagent grade water (18.2 MΩ-cm resistivity), obtained froma Sartorius Arium Comfort combined water system. pH determinations were made with a Hanna HI 9124 waterproof pH meter. Glassy carbon foil substrates (Carbon-Vitreous 3000C (C) foil, 1.0 mm thickness) were obtained from GoodFellow. All other materials were obtained as stated in the text. Experiments performed at “room temperature” were carried out at 20 °C.

**SI-2: Electrochemical Methods: General:** Electrochemical studies were performed in a three-electrode configuration (unless otherwise stated) using a CH Instruments CHI760D potentiostat. Strips of graphite sheet were used as the counter electrode and were not re-used. Ag/AgCl (NaCl, 3 M, from both BASi and CH Instruments) and Hg/Hg2SO4 (saturated K2SO4, CH Instruments) reference electrodes were used as specified. A glassy carbon button electrode was used as the working electrode (unless otherwise stated) except when preparing samples for SEM and XPS analysis, in which case a piece of glassy carbon foil was used. Both working and counter electrodes were washed with acetone and deionized water prior to use. Three-electrode potentials were converted to the NHE reference scale using *E*(NHE) = *E*(Ag/AgCl) + 0.209 V and *E*(NHE) = *E*(Hg/ Hg2SO4) + 0.658 V.

**Bulk electrolysis:** Bulk electrolyses were performed in a three-electrode configuration (unless otherwise stated) in two-compartment electrochemical cells unless otherwise stated, the compartments of the H-cell being separated by a 0.180 mm-thick Nafion N-118 membrane, with this membrane being held in place by judicious application of Araldite epoxy glue (Bostik Findley, Ltd., UK). Solutions were stirred, keeping the same stirring rate for all experiments. Where voltages have been corrected for ohmic resistances, the effective voltage (Veffective) is given by:S[[1]](#endnote-2)

Veffective = Vapplied – *i*R

where *i* is the current flowing through the cell and R is the resistance of the cell. Cell resistances were measured by the *i*R test function available on the CH potentiostats, using the general method developed by He and Faulkner.S[[2]](#endnote-3) Briefly, the *i*R test function works by examining the current response to small step changes in voltage relative to a test potential at which no faradaic current flows. In our case, the step change (ΔV) was 0.05 V and the test potential was selected as 0 V *vs.* Ag/AgCl. The *i*R test function on the potentiostat then extrapolates the signal-averaged currents at 54 and 72 ps after the voltage-step edge backwards to obtain a current at *t* = 0, where this current can also be expressed as ΔV/R. R in this case is the solution resistance that is sought. The final parameter that the user must select with this function is the acceptable stability limit of the system at the value of R measured (“% overshoot”): in our case a value of 2% was chosen (default setting on the potentiostat). The error associated with this *i*R-correction is dominated by the error associated with gauging the resistance of the solution, where values were found to vary over a range of Rmeasured ± 3%.

**Stripping Voltammetry:** Prior to stripping voltammetry, glassy carbon working electrodes (area = 0.071 cm2) were first decorated with silver by running bulk electrolyses using such an electrode, an Ag/AgCl reference electrode and graphite counter electrode in 2-compartment cells in 1 M H2SO4 at −0.54 V *vs.* RHE for various times, such that different current densities for hydrogen evolution were obtained. Once the desired current density had been reached, electrolysis was terminated and the working electrode was removed from solution and washed carefully with deionized water. The decorated electrode was then immersed in fresh 1 M H2SO4 in a two-compartment cell. The working electrode compartment was further equipped with an Hg/Hg2SO4 reference electrode and was stirred. The counter electrode compartment was equipped with a graphite counter electrode. Stripping voltammograms were then collected at room temperature at a scan rate of 5 mV/s, starting from −0.4 V *vs.* Hg/ Hg2SO4. Measurements were conducted without *i*R compensation. A second scan was performed in all cases to ensure that all the Ag had been stripped in the first scan. The loading of silver on the electrode surface was then obtained by integrating the peak occurring between −0.2 V and +0.1 V *vs.* Hg/Hg2SO4 in the stripping voltammogram to find the total charge passed during stripping. This was converted to a number of moles of Ag(0) stripped from the surface by dividing this charge by Faraday’s constant (assuming a monoelectronic oxidation of Ag(0) to Ag+ under these conditions).

**Tafel Plots:** Glassy carbon working electrodes (area = 0.071 cm2) were subjected to bulk electrolysis applying −0.54 V *vs*. RHE in a 2-compartment cell in 1 M H2SO4 in the presence of an Ag/AgCl reference electrode until the current density reached a value of between 1-2 mA/cm2. A graphite counter electrode was used. Immediately after the end of electrolysis, and without changing anything in the experimental set-up, Tafel plots were obtained by linear sweep voltammetry, sweeping the potential from −0.51 V to −1.0 V *vs.* Ag/AgCl at a scan rate of 2 mV/s with stirring. A repeat scan under the same conditions gave an essentially identical result.

**Bulk electrolysis activity tests with a pristine Ag/AgCl reference electrode:** A clean and freshly-polished glassy carbon working electrode (area = 0.071 cm2) was subjected to bulk electrolysis applying −0.54 V *vs*. RHE in a 2-compartment cell in the presence of a pristine Ag/AgCl reference electrode and a graphite counter electrode overnight. A range of electrolytes was screened in this way: 1 M sulfuric acid, 1 M phosphoric acid, 1 M potassium phosphate buffer (pH 7), 1 M potassium borate buffer (pH 9.2) and 1 M sodium phosphate buffer (pH 12). After this overnight electrolysis, the working electrode was again thoroughly cleaned and polished, in order to remove any silver deposited on its surface. Meanwhile, the reference electrode was rinsed and a new counter electrode was obtained. The cleaned glassy carbon working electrode was then subjected to bulk electrolysis applying −0.54 V *vs*. RHE in a 2-compartment cell in the presence of the Ag/AgCl reference electrode and a graphite counter electrode in fresh 1 M sulfuric acid. The profile of the resulting current density *vs.* time profile in 1 M sulfuric acid was then compared to that obtained for the pristine Ag/AgCl reference electrode during its first use in 1 M H2SO4.

**Calibration of Reference Electrodes:** Reference electrodes were calibrated versus a master reference electrode used only for this purpose, according to a procedure on BASI’s website.S[[3]](#endnote-4) Briefly, the master reference electrode and the reference electrode to be checked were immersed in 3 M NaCl solution. The master reference was connected to a potentiostat’s reference electrode cable and the Ag/AgCl electrode undergoing calibration was connected to the working electrode cable. The open circuit potential between the two electrodes was then measured. Ideally the difference between the two electrodes should be zero, but a value ±20 mV is considered by the suppliers as within the error of this type of electrode.

**SI-3: Headspace Hydrogen Determination:** Gas chromatography was conducted in airtight single-chamber and 2-compartment cells using 1 M H2SO4 as the electrolyte and an Ag/AgCl reference electrode, using an Agilent Technologies 7890A GC system. During electrolysis, the solution was stirred and the headspace was sampled by gas-tight syringe (volume taken per sampling event = 25 µL) and introduced onto the GC column by direct injection at various intervals. The column used was a 30 metre-long 0.320 mm widebore HP-molesieve column (Agilent). The GC oven temperature was set to 27 ºC and the carrier gas was Ar. The front inlet was set to 100 °C. The GC system was calibrated for H2 using certified standards of hydrogen at a range of volume % in argon supplied by CK Gas Products Limited (UK). Linear fits of volume % *vs.* peak area were obtained, which allowed peak areas to be converted into volume % of H2 in the cell headspace. Total system headspaces were calculated by filling the cells with water at room temperature. Typical headspaces were on the order of 113 mL for the single chamber cell and 11 mL for the 2-compartment cell. Charges passed were converted into expected volume percentages of hydrogen in the headspace by converting charges to an expected number of moles of gas (by dividing by 2*F* for H2, where *F* is the Faraday constant), and then taking the volume of 1 mole of an ideal gas at room temperature and pressure to be 24.5 L. Faradaic efficiencies were then calculated by taking the ratio of gas volume % based on the charge passed to the gas volume % measured by gas chromatography. Faradaic efficiencies were based on the total amount of charge passed, uncorrected for any background or capacitance currents. All gas determinations were performed three times, and average Faradaic efficiencies are reported in the main text (see also representative GC data in Figure S1).

**SI-4: Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX).** Scanning electron microscopy was performed with a Philips XL30 ESEM instrument equipped with an Oxford Instruments Energy 250 energy dispersive spectrometer system at an acceleration voltage of 25 kV. Following electrolysis experiments on glassy carbon foil, the electrodes were rinsed gently with deionized water and allowed to dry in air before loading onto 12 mm AGAR scientific conductive carbon tabs. Images and EDX spectra were obtained with acceleration voltages between 12 kV and 20 kV. Spectra were analysed using Oxford Instrument INCA 4.09 Microanalysis Suite – Issue 17b.

**SI-5: X-ray photoelectron analysis (XPS).** Following electrolysis, the electrodes were rinsed gently with deionized water and allowed to dry in air. These electrodes were then carefully packed and sent to the National EPSRC XPS Users' Service (NEXUS) at Newcastle University, UK. XPS spectra on glassy carbon substrates (Carbon-Vitreous 3000C (C) foil, 1.0 mm thickness, GoodFellow) were acquired with a K-Alpha instrument (Thermo Scientific, East Grinstead, UK), using a micro-focused monochromatic AlKα source (X-ray energy 1486.6 eV). Three positions were analyzed per sample. The resulting spectra were referenced to the adventitious C 1s peak (285.0 eV) and were analyzed using the free-to-download CasaXPS software package.

1. S Hamann, C. H.; Hamnett, A.; Vielstich, W. *Electrochemistry* (2nd. Edition). Wiley-VCH, Weinheim, 2007. [↑](#endnote-ref-2)
2. S He, P.; Faulkner, L. R. Intelligent, Automatic Compensation of Solution Resistance. *Anal. Chem.* **1986**, *58*, 517-523. [↑](#endnote-ref-3)
3. S https://www.basinc.com/manuals/LC\_epsilon/Maintenance/Reference/ reference#testing (accessed October, 2016). [↑](#endnote-ref-4)