

Research



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Author for correspondence:

Enyi Guo

e-mail: enyi.guo@sydney.edu.au

A post Gurney quantum mechanical perspective on the electrolysis of water: ion neutralization in solution

Enyi Guo^{1,2} and David R. McKenzie^{1,2}

¹School of Physics, and ²Australian Institute for Nanoscale Science and Technology, University of Sydney, Sydney, New South Wales 2006, Australia

EG, 0000-0003-3825-5343; DRM, 0000-0002-2476-1301

Electron fluxes crossing the interface between a metallic conductor and an aqueous environment are important in many fields; hydrogen production, environmental scanning tunnelling microscopy, scanning electrochemical microscopy being some of them. Gurney (Gurney 1931 *Proc. R. Soc. Lond.* **134**, 137 (doi:10.1098/rspa.1931.0187)) provided in 1931 a scheme for tunnelling during electrolysis and outlined conditions for it to occur. We measure the low-voltage current flows between gold electrodes in pure water and use the time-dependent behaviour at voltage switch-on and switch-off to evaluate the relative contribution to the steady current arising from tunnelling of electrons between the electrodes and ions in solution and from the neutralization of ions adsorbed onto the electrode surface. We ascribe the larger current contribution to quantum tunnelling of electrons to and from ions in solution near the electrodes. We refine Gurney's barrier scheme to include solvated electron states and quantify energy differences using updated information. We show that Gurney's conditions would prevent the current flow at low voltages we observe but outline how the ideas of Marcus (Marcus 1956 *J. Chem. Phys.* **24**, 966–978 (doi:10.1063/1.1742723)) concerning solvation fluctuations enable the condition to be relaxed. We derive an average barrier tunnelling model and a multiple pathways tunnelling model and compare predictions with measurements of the steady-state current–voltage relation. The tunnelling barrier was found to be wide and low in agreement with other experimental studies. Applications as a biosensing mechanism are discussed that exploit the fast tunnelling pathways along molecules in solution.

1. Introduction

The charge transfer processes that occur when water is placed between metallic electrodes to which voltage is applied, are relevant in many applications including electrolysis of water for hydrogen production [1], hydroxyl radical production for water purification [2], scanning tunnelling microscopy (STM) under water, scanning electrochemical microscopy (SECM) [3] in aqueous environments, biosensing of molecular interactions at interfaces [4] and the storage of energy in capacitors. The charge transfer processes occurring at the electrode surfaces determine the voltage–current relation, which is central to all of these applications. The current responses taking place for a fixed voltage may be divided into two classes: transient responses with timescales generally shorter than seconds and quasi steady-state responses with timescales generally longer than minutes. The transient current flows are traditionally ascribed to ion diffusion that results in the establishment of charged layers known as *double layers* in the vicinity of the electrode surfaces. The steady-state currents usually referred to as electrochemical or ‘Faradaic’ currents, are related to electrolysis and are usually ascribed to charge transfers to or from ions adsorbed onto the electrode surfaces [5]. At sufficiently large current densities, the electrochemical processes lead to water electrolysis that results in molecular hydrogen evolution at the cathode that has been ascribed to the Volmer, Heyrovsky and Tafel reactions [6]. Here we are interested in electron tunnelling into solution as originally envisaged by Gurney in 1931 [7] and in determining whether there are conditions under which it is rate limiting and therefore responsible for the current–voltage characteristics of water electrolysis. The essential ideas of the Gurney theory [7,8] have been briefly summarized by Anderson and Albu [9] as follows: the predicted electrode current in one direction is proportional to a three-term product of the energy distribution function of the electrons in the electrode surface, the energy level distribution function of the ions in solution and the tunnelling probability which in turn depends on the electron kinetic energy and the tunnelling distance.

A great deal of new science surrounding tunnelling has been discovered since the work of Gurney. The advent of STM operating in aqueous environments in which a tip and a surface are immersed in water in close proximity, has led to the acceptance of electron tunnelling through water as a charge transfer process [1,2]. The tunnelling mechanism, if it applies to electrolysis, would release neutral atoms in water some distance away from the electrodes and may be a mechanism for nanobubble formation in solution [10]. At the cathode, the hydronium ion would be neutralized by a tunnelling electron to form the hydronium radical which would subsequently decay into water and hydrogen. Confirmation that large electric fields are present in the double layers near electrodes, even at low voltages in pure water, adds further weight to the hypothesis that Gurney-type tunnelling behaviour may be present at low voltages in pure water [11].

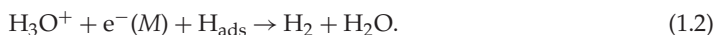
We chose gold electrodes for an experimental study of low-voltage currents in water because it is inert and forms a stable coating on stainless steel. Field-assisted tunnelling was discussed in the seminal work of Fowler & Nordheim [12] and has been used to describe tunnelling in STM. In the language of STM, tunnelling at the cathode in electrolysis would be an *empty state* electron tunnelling process from the electrode to an empty state in a hydronium ion and at the anode a *filled state* tunnelling process would occur from a filled state in a hydroxide ion to an empty state in the electrode. Both of these processes take place in the presence of an electric field in the double layers, which is expected from theory to be approximately equal at the cathode and anode [11].

The science of the electrolysis of water has a long history, dating back to the work of Nicholson and Carlisle in 1800, predating Faraday who named the phenomenon. Universal agreement as to the nature of the rate-limiting process that determines the current–voltage relation in electrolysis has not yet been achieved, even for the simplest case, that of pure water between noble metal electrodes, the case of interest here. The reactions for the neutralization of the hydronium ion at the cathode and of the hydroxide ion at the anode have been proposed to involve electron transfer between the metal and ions that are adsorbed to the surface. At the cathode surface, the capture

of an electron from the metal (M) is proposed by the Volmer reaction:



or the Heyrovsky reaction [13]:



At the anode, a hydrated hydroxide ion present on the surface, would release an electron to the metal:



Under an electron tunnelling hypothesis, the reaction at the cathode would be the formation of a hydronium radical from a hydronium ion and its subsequent decay via reactions such as:



and



and at the anode the hydrated hydroxide ion would release an electron to the anode. The electric fields will only be exactly equal at the cathode and anode in the steady-state regime if the two tunnelling steps require the same electric field to achieve the same rate. Otherwise, a stronger field would be necessary at the electrode where the reaction requires the larger driving force.

In pure water, ions arise from the spontaneous proton exchanges between water molecules that form hydronium and hydroxide ions. A complication arises from dissolved atmospheric gases, especially carbon dioxide, that forms carbonate and bicarbonate ions as well as some additional hydronium ions. The initial current arising in the transient response upon the application of voltage to electrodes obeys Ohm's law:

$$J = \sigma E, \quad (1.6)$$

where J is the current density, E is the macroscopic electric field present in the water and σ is the conductivity. The conductivity during the transient behaviour is determined by the concentration of ions and their drift mobilities. For applied potential differences of less than a few volts, the current decreases greatly and almost immediately as ions accumulate in boundary layers at the surfaces of the electrodes, reducing the electric field in the bulk of the water and concentrating it in the boundary layers. The relation between voltage and the steady-state tunnelling current is non-ohmic in observations made using the STM both in vacuum and under water [14].

The steady-state current-voltage relation for the current flowing between electrodes in aqueous solutions has been known to be non-ohmic for a long time. Caspari in 1899 described the non-ohmic nature of the current flowing between inert electrodes in dilute acid solutions in water [15]. Tafel in 1905 found a linear relation between the logarithm of current and the potential difference between electrodes [16]. Bowden in 1929 made extensive studies of the currents flowing at small applied voltages [17]. The applied voltage V was found empirically to be related to the current i by the equation named after Tafel:

$$V = A \ln \left(\frac{i}{i_0} \right), \quad (1.7)$$

where A and i_0 are constant. When a scanning tunnelling microscope is operated in water, the current flowing between the atomically sharp metal point and the sample is a function of the distance from the point to the sample. The current initially falls rapidly, approximately exponentially with distance and then reaches a plateau value at larger distances. Moon-Bong Song *et al.* have examined the dependence of the plateau current at large distances on the potential difference between the tip and the sample and found it to be non-ohmic [14].

In the present work, we will obtain time- and voltage-dependent measurements and test them against the Gurney theory, taking advantage of recent progress in finding the hydronium and hydroxide ion densities in water from theory as a function of applied voltage and time. The aim

of the work is to confirm or deny Gurney's original idea that there is a contribution to electrolysis in water from the tunnelling of electrons to and from ions in solution.

2. Materials and methods

Water was obtained from a Millipore Direct-Q3 purification system with a new ion exchange stack. Water is dispensed from this unit only if the measured resistivity exceeds $18\text{ M}\Omega\text{ cm}$. The test cell used for the measurement of the time-dependent current in this work has two parallel plate electrodes as shown in figure 1. The system allows the space between the electrodes to be kept full of water and to allow any gas bubbles to be removed from the space between the electrodes. Water directed from the purification system was directed to the test cell via airtight plastic tubing. Flushing of the cell cavity was sustained until the last visible bubble was observed to exit the cell. The cell reservoir was covered by a glass Petri dish forming a 'seal' to minimize air contact. A measurement of the conductivity of the water supplied by the ion exchange stack and without exposure to the atmosphere using this cell gives a typical value of $20.1 \pm 1.80\text{ M}\Omega\text{ cm}$ at 22°C . This value compares well with the accepted value of the resistivity of pure water arising from the auto-dissociation into hydronium and hydroxide ions of $18.18 \pm 0.03\text{ M}\Omega\text{ cm}$ at 25°C [18]. Atmospheric carbon dioxide was excluded from the measurements for pure water by streaming the water directly from the purification system without contact with the atmosphere. Carbon dioxide exposure has a strong effect on the conductivity through the creation of additional hydronium ions with carbonate and bicarbonate anions. After exposure to the atmosphere, we find a decrease in resistivity to values less than $3\text{ M}\Omega\text{ cm}$. One study has reported a resistivity of $1\text{ M}\Omega\text{ cm}$ at an ambient CO_2 concentration of 500 ppm [19]. Our measurements were done in a concentration of approximately 395 ppm [20], the global average concentration in 2014, the year our measurements were done. Therefore, our measurements of conductivity in atmosphere exposed water are considered to be in agreement with the reported values.

Measurements of the voltage drop at the electrode–water interfaces were carried out by adding an extra probe in the water, symmetrically located between the electrodes. Potential falls across the half cells were measured simultaneously with Agilent U1233A and Digitor Q1467 multimeters. In order to test the effect of the individual meters, they were interchanged and the measurement repeated.

The time-dependent current was measured using a Keithley 617 electrometer connected to a Tektronix TDS 2002B oscilloscope for current display. The current transients were recorded when the voltage was applied (the *switch-on transient*) and when it was removed (the *switch-off transient*) and the source of emf replaced by a short circuit, using the circuit containing a single pole double throw (SPDT) switch shown in figure 1. The two current transients are opposite in direction and have similar shape, representing the charging and discharging of the double-layer capacitors formed between the bulk liquid and the electrode surfaces. Water was at equilibrium with ambient atmosphere and cavity was flushed with it in between 45 s and 100 s current transient recordings.

In order to achieve electrolysis in water at a readily observable rate, a minimum voltage is required as a result of the presence of potential barriers for the transfer of electrons [21]. A value of 1.23 V is considered to be this threshold voltage [22]. In our experiments, the voltage was kept below a maximum voltage of 1.20 V to ensure that the barrier was not likely to be overcome in the classical sense so that quantum mechanical tunnelling is necessary. A set of voltages from 0 V to 1.20 V at 0.05 V intervals was applied to directly feed pure water and pure water left exposed to room air overnight. Each test voltage was maintained for 150 s until switch-off, at this time point the current drops to a relatively stable level and the reading is taken before switch-off. Three sets of identical measurements were taken in quick succession for each sample of water to measure average current and its uncertainty. Flushing of the cell cavity was performed in between each applied voltage to maintain the purity of water. Such a procedure was not required during tests using water exposed to environmental CO_2 , however periodic flushing was still performed to remove the small bubbles that are observed to form in the cavity.

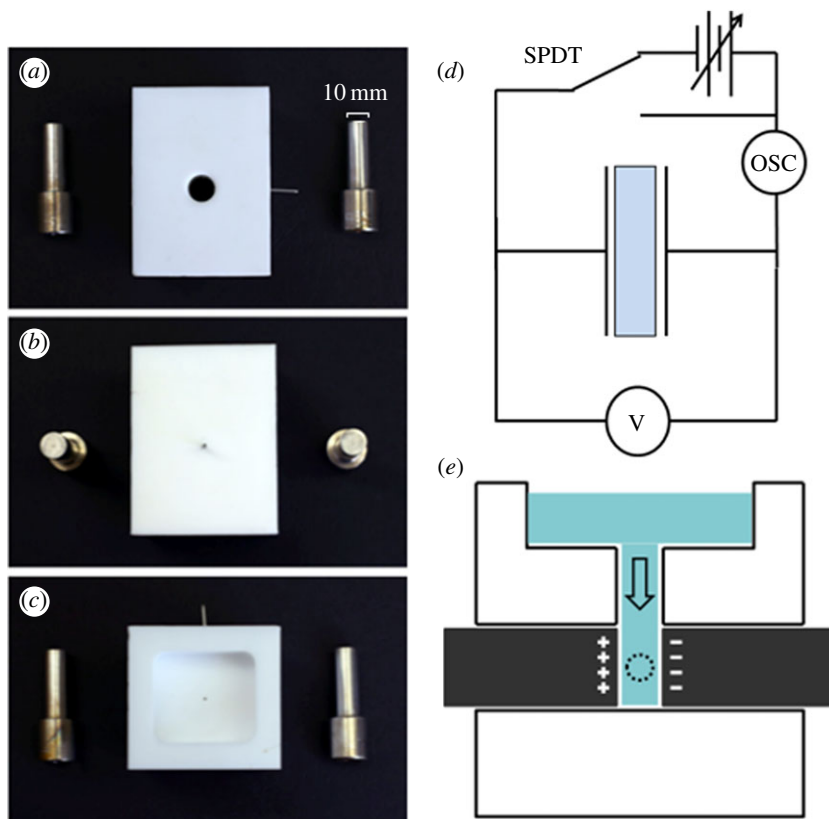


Figure 1. Circuit diagrams and photographs of the apparatus for measuring the time-dependent current between two gold-coated electrodes immersed in a medium of pure water flowing from a deionized water reservoir. (a) Side view showing the cylindrical cavity for electrodes. (b) Front view showing the guide tube for water exit and top view of uncoated stainless steel electrode flat surfaces. (c) Top view showing the reservoir and hole for water entry. (d) The adjustable DC voltage power supply is connected through a SPDT switch to the cell in series with an electrometer whose output is connected to an oscilloscope. The alternative position of the switch short circuits the cell through the electrometer. (e) Water is drawn through the cavity by a mini roller pump connected to the guide tube represented by the dashed circle.

3. Results and discussion

Steady-state current–voltage measurements are plotted in [figure 2](#) as a dependence of the applied voltage on the logarithm of the current for pure water and water exposed to the atmospheric CO_2 . The applied voltage is halved to give the voltage drop across half of the cell, since the voltage drops are symmetrical about the centre of the water gap ([figure 3](#)). The Tafel relation of equation (1.7) predicts a linear relation for this plot. While the data approximate a linear Tafel plot in the high-voltage regions, there are strong deviations at low voltages, showing that the physics of the phenomena are not captured by the conventional Tafel equation.

(a) Estimating the fraction of surface adsorbed charge from the transient current response

The voltage drops across the double layers at each electrode in the steady state relative to a symmetrically located central electrode for CO_2 -exposed water were found to be equal within the accuracy of the measurement ([figure 3](#)) at four voltages across the scale. The observation of an equality of the voltage drops at the cathode and anode agrees with the calculations of Morrow & McKenzie [11].

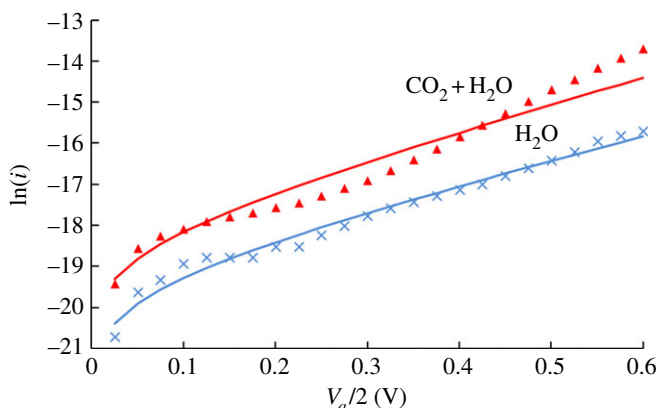


Figure 2. The dependence of the voltage drop at one electrode $V_a/2$ in volts relative to the centre of the water gap on the logarithm of the current i in ampere. The points are experimental data for CO_2 -exposed water (triangles) and for pure water (crosses). The lines are fits using the multiple pathways model (see §3b) and show that the model only fits the simplest case of pure water. (Online version in colour.)

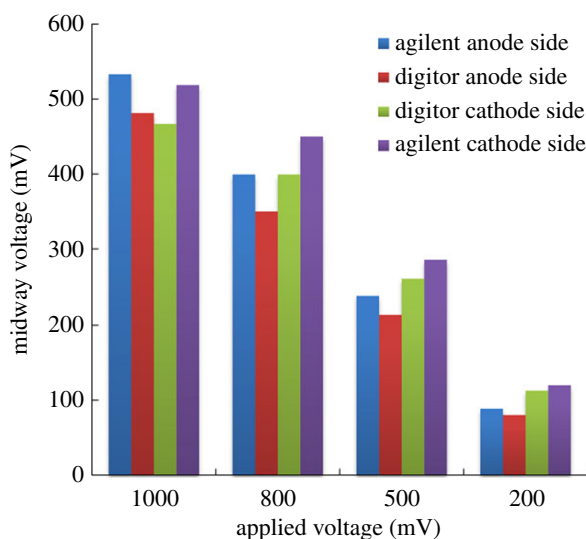


Figure 3. Magnitude of the voltage at a symmetrically located electrode between the cathode and the anode in CO_2 -exposed water. Measurements made with an Agilent meter on the anode side and a Digitor meter on the cathode side are shown as blue and green columns, respectively. Meters were swapped after each measurement to obtain a new set of measurements shown as red and purple columns. The meter type did not significantly influence the reading.

The time-dependent current is shown in figure 4 for CO_2 -exposed water as a function of time after the initial switching on of the power supply for either 45 or 100 s and then throwing the SPDT switch to replace the power supply with a short circuit. In the *switch-on transient*, there is a large, rapidly varying current that we attribute to the motion of ions, leading to the accumulation of a charge Q in the vicinity of the electrodes. At long times, the steady-state current is observed that we attribute to the tunnelling current. In the *switch-off transient*, most of the accumulated charge is lost during a reverse current transient while at long times, a steady-state current is observed which we attribute to tunnelling to adsorbed ions on the electrode surfaces. The steady-state current after switch-off, unlike the transient, is in the same direction as the switch-on current but

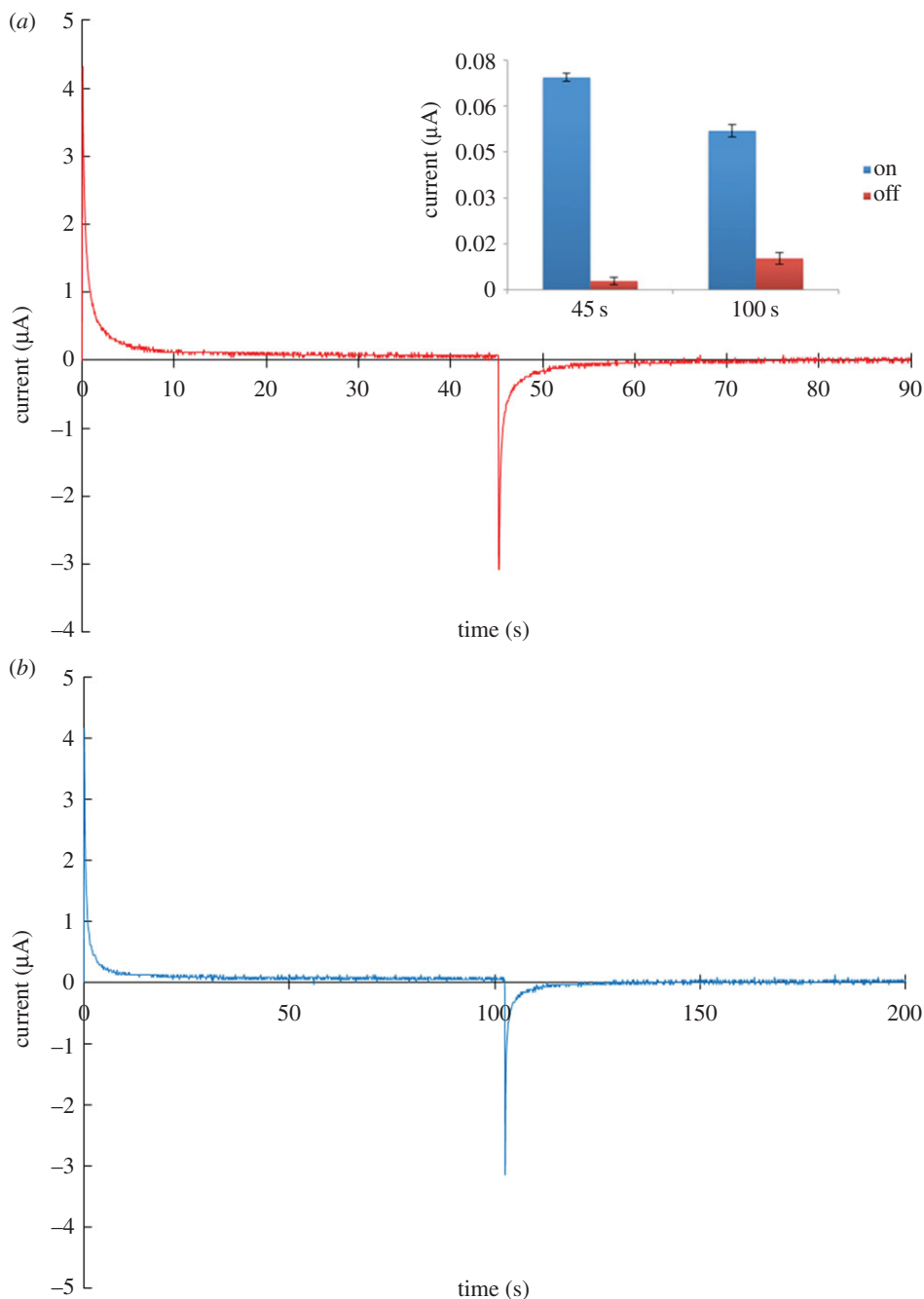


Figure 4. The current trace as a function of time after voltage is applied for the first time to gold electrodes in pure water showing the *switch-on transient* during the application of 0.4 V for 45 s (a) or 100 s (b), after which the voltage is switched to zero, giving a *switch-off transient*. The persistent current at long times in both cases attributed to tunnelling to and from ions either in solution or attached at the electrodes. The inset shows the difference in steady current (averaged over the last 10 s) for switch-on and switch-off (left and right columns, respectively) for transients lasting for 45 and 100 s. The steady tunnelling current at switch-on includes tunnelling to both ions in solution and adsorbed ions and is larger than the steady current at switch-off which is due to tunnelling to adsorbed ions only.

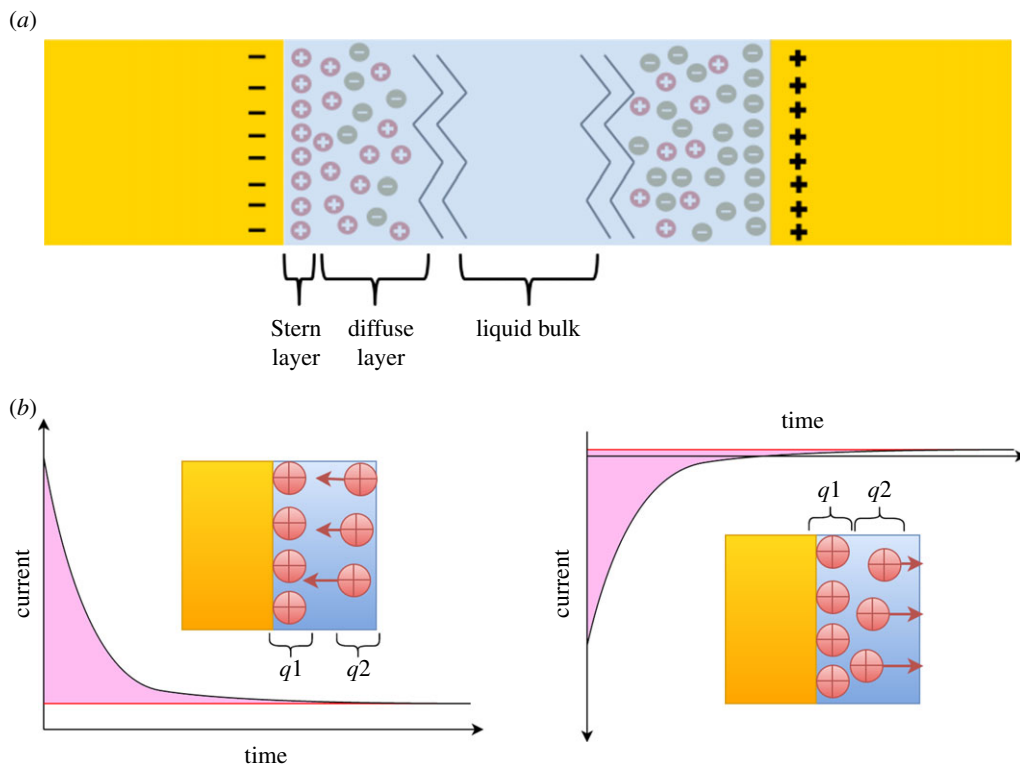


Figure 5. (a) A schematic of gold electrodes immersed in pure water showing the ion configuration. The positive charges in solution represent solvated hydronium ions and the negative charges represent solvated hydroxide ions. The blue shading indicates neutral water molecules. (b) The interpretation of the contributions to the switch-on and switch-off transients with insets indicating ion movement near the cathode surface and charge classification. The pink area of switch-on represents Q , the sum of $q1$ and $q2$ and the pink area of switch-off represents only $q2$, while the red lines are the corresponding steady state on and off currents shown in the inset for 100 s after switch-off.

with a smaller magnitude. The magnitudes of the steady-state currents are compared in the inset to figure 4.

In order to interpret the results of figure 4 further, we now discuss the structure of the layers near the electrodes when voltage is applied to them. We assume, as illustrated schematically in figure 5a that the accumulated charge Q , is equal to the sum of the charge $q1$ in the adsorbed layer also known as the *Stern layer* [23] and the charge $q2$ in the *diffuse layer*, which is dissipated during the switch-off transient.

Figure 5b illustrates how the charge in each category is calculated and the motion of charges in that category. The pink area of the switch-on represents the total charge Q accumulating in solution at each electrode. The pink area of switch-off represents the charge $q2$ that moves away from the cathode. The adsorbed charge $q1$ remains on the surface to be progressively neutralized at the electrode surface, leading to the quasi-steady-state current that is observed at long times after switch-off. The steady-state current at switch-on is larger than at switch-off because some of the current after switch-on is caused by electron tunnelling to and from ions in the *diffuse layer*, whereas after switch-off the ions in the *diffuse layer* have moved away and are not able to participate in electron tunnelling.

Table 1 gives the amount of charge in each category discussed above, using the current at 100 s as the best estimate of the quasi-steady-state current. Two estimates of each quantity are available, one from the integrated current of the 45 s transient and the other from the integrated current for the first 45 s of the 100 s transient. The adsorbed charge $q1$ is obtained from the difference between

Table 1. Total charge Q , adsorbed charge q_1 and accumulated solution charge q_2 obtained from the *switch-on* and *switch-off* transients for 45 s delay between switch-on and switch-off, the first 45 s of the data for 100 s delay, and for 100 s delay.

time	Q (C)	q_1 (C)	q_2 (C)	q_1/area ($e \text{ nm}^{-2}$)
45 s	4.95×10^{-6}	1.97×10^{-6}	2.98×10^{-6}	0.015
1st 45 s of 100 s	5.08×10^{-6}	1.98×10^{-6}	3.09×10^{-6}	0.016
100 s	5.54×10^{-6}	2.29×10^{-6}	3.25×10^{-6}	0.018

the total accumulated charge Q and the charge q_2 which is lost during switch-off. Note that the adsorbed charge q_1 represents approximately 40% of the total accumulated charge Q . Under the conditions we use, there is much less than one ion adsorbed per square nanometre as observed from table 1.

(b) An average tunnelling barrier model for calculating barrier dimensions

Useful expressions have been obtained by Simmons for the tunnelling current between two conductors separated by an insulating layer [24]. The expressions were derived with applications in the solid state in mind, but are generally applicable to any tunnelling problem, within the limits of the WKB approximation. The current density was found to be:

$$J = J_0 \left\{ \bar{\varphi} \exp \left(-A\sqrt{\bar{\varphi}} \right) - (\bar{\varphi} + eV) \exp \left[-A\sqrt{\bar{\varphi} + eV} \right] \right\}, \quad (3.1)$$

where

$$J_0 = \frac{e}{2\pi h(\beta \Delta s)^2}, \quad A = \frac{4\pi\beta \Delta s \sqrt{2m}}{h}$$

and β is a constant of order unity. $\bar{\varphi}$ is the average barrier height and Δs is the barrier width which is somewhat smaller than the thickness s of the insulator across which tunnelling is taking place. The effective barrier width is slightly reduced because of the induction of image charges in the electrodes that cause a rounding of the edges of the barrier and strongly reduced at large applied voltages because of the effects of the electric field. Equation (3.1) can be reduced to simpler forms in two cases, one for low voltages defined by $eV \ll \bar{\varphi}$ for which the current density given by:

$$J = \frac{e^2 \sqrt{2m}}{h^2} \sqrt{\varphi_0} \exp \left(-\frac{4\pi s \sqrt{2m}}{h} \sqrt{\varphi_0} \right) E, \quad (3.2)$$

where φ_0 is the barrier height at the electrode and the electric field is $E = V/s$. In this regime the average barrier height $\bar{\varphi}$ is equal to φ_0 and also, the barrier thickness is independent of the applied field and the approximation that $\Delta s = s$ is made. The other case is the high-voltage regime where $eV \gg \bar{\varphi}$ for which the current density is:

$$J = \frac{2.2e^3 E^2}{8\pi h \varphi_0} \left[\exp \left(-\frac{8\pi \sqrt{2m}}{3heE} \varphi_0^{\frac{3}{2}} \right) \right]. \quad (3.3)$$

In this regime, the effective barrier width is given by $\Delta s = \varphi_0/eE$ and the average barrier height is $\bar{\varphi} = \varphi_0/2$. When this approach is applied to our electrolysis problem, given the assumed symmetry of the voltage drops, there will be two identical barriers connected in series through the bulk water acting as a conductive connecting medium. If we make the assumptions that tunnelling is the rate-limiting process and that the barrier can be represented by an average over all time and spatial variations, the expressions of Simmons can be applied to the measured current and half of the applied voltage, enabling us to calculate barrier dimensions assuming that tunnelling is the rate-limiting process. We multiply current densities in equation (3.3) with electrode area A_{eff} , and then rearrange the high-voltage equation of Simmons to obtain an

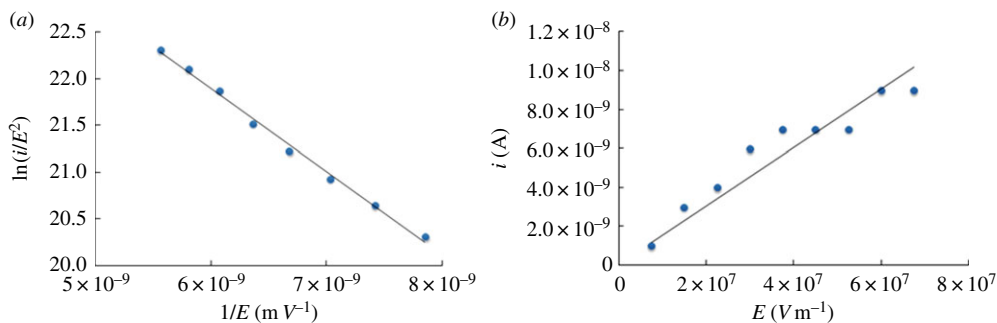


Figure 6. A fit of the data for $\ln(i/E^2)$ pure water according to the high-voltage equation (3.4) after converting the experimental voltage values to electric fields using the conversion factor $1.5 \times 10^8 \text{ m}^{-1}$ (a). The corresponding fit of the data for current i using low-voltage equation (3.5) to the experimental data using the same conversion factor (b). (Online version in colour.)

equation that shows a linear dependence:

$$\ln\left(\frac{i}{E^2}\right) = \ln\left(\frac{2.2A_{\text{eff}}e^3}{8\pi\hbar\varphi_0}\right) + \left(\frac{-8\pi\sqrt{2m}\varphi_0^{3/2}}{3\hbar e}\right) \frac{1}{E}. \quad (3.4)$$

Similarly, we calculate total current i for the low-voltage region from equation (3.2) giving:

$$i = \frac{A_{\text{eff}}e^2\sqrt{2m\varphi_0}}{\hbar^2} \exp\left(\frac{-4\pi s\sqrt{2m\varphi_0}}{\hbar}\right) E. \quad (3.5)$$

In order to apply these equations to the electrolysis problem, we need to determine the electric field present at the electrodes where tunnelling is occurring. Assume the electric field is proportional to the applied voltage by a proportionality factor F_E . The electric field at a position very close to the gold surface but outside the immediately adsorbed charges on the surface is found using the information in table 1. The surface carries a charge Q that is opposite in sign to the adsorbed charge q_1 . Therefore, the net charge that creates the field in the solution nearby is numerically the same as q_2 but opposite in sign. From Gauss' law, the electric field is given by:

$$E = \frac{-q_2}{\epsilon_r\epsilon_0 A_{\text{eff}}}, \quad (3.6)$$

where ϵ_r is the static relative dielectric constant of water. From the values of table 1 for an applied voltage of 0.4 V and assuming the relative dielectric constant of water is 78 at 25°C a value of F_E of approximately $1.5 \times 10^8 \text{ m}^{-1}$ is obtained.

The gradient of the high-voltage expression after fitting to the experimental results enables the evaluation of φ_0 after using the electric field formula equation (3.4). Linear plots shown in figure 6 and figure 7 are made with the field version of high- and low-voltage equations. Then the calculated φ_0 and the gradient of the low-voltage fit are introduced to the low voltage regime formula equation (3.5) to calculate barrier width s .

The results have been tabulated in the table 2 where the dimensions of the rectangular barriers are compared for the two types of water sample investigated in this study. Standard errors for the average over three consecutive trials are not considered when performing the linear fit for CO_2 -exposed water because the differences in barrier heights and widths are less than 1%. Schmickler noted that experimental values for the effective barrier height for electron tunnelling through water fall into two classes; low values in the range of a few tenths of an electron volt and higher values of 1–2 eV [25]. For example, Halbritter *et al.* have made measurements of effective tunnelling barrier heights using STM under water [26]. They proposed that the low barrier heights in the range from 0.14 to 0.35 eV are a consequence of *intermediate states* originating from 'dipole resonances' in water. Peskin *et al.* have proposed that there are energy states (up to 1 eV below the vacuum energy) that may be associated with 'structural cavities' in the water [27]. The presence

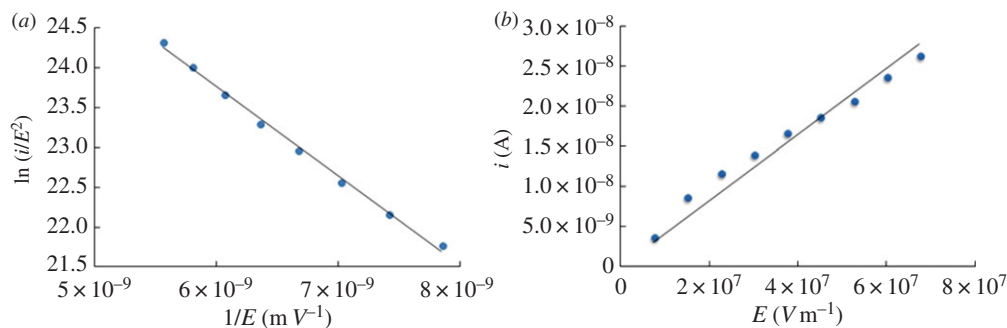


Figure 7. A fit of the data for $\ln(i/E^2)$ CO_2 -exposed water according to the high-voltage equation (3.4) after converting the experimental voltage values to electric fields using the conversion factor $1.5 \times 10^8 \text{ m}^{-1}$ (a). The corresponding fit of the data for current i using low-voltage equation (3.5) to the experimental data using the same conversion factor (b). (Online version in colour.)

Table 2. The heights φ_0 and widths s of tunnel barriers for pure water and CO_2 -exposed water obtained using the average barrier model of equations (3.4) and (3.5).

	H_2O	$\text{H}_2\text{O} + \text{CO}_2$
φ_0 (eV)	0.26 ± 0.01	0.30 ± 0.01
s (nm)	7.09 ± 0.08	6.38 ± 0.06

of these low-energy intermediate states, illustrated in figure 9 by local minima, leads to lowered effective barrier height. Since in our experiment, both electrodes have a large spatial extent, the barrier should be considered as having a three-dimensional structure that varies with position on the electrode surface at a fixed time and as well it varies with time as molecular motion takes place. The effective barrier height is a weighted average over the whole surface, where the weighting is biased towards the lower barrier heights, which have the higher transmission probability. It is therefore expected that large area electrodes would give a greater opportunity for tunnelling ‘hotspots’ than would be present for the small tip of an STM. The barrier heights we show in table 2 are consistent with the lower values obtained by Halbritter *et al.* supporting the idea of intermediate states that lower the average barrier height.

(c) Steady-state field distribution in water near an electrode

When constant voltage is applied to electrodes in water, the steady state in the distribution of ions is reached when ions enter the ion accumulation region near the electrodes at a rate just sufficient to replace losses. Losses of ions occur when they are neutralized by the tunnelling of electrons between the ion and the electrode surface. The steady-state electric field and ion distributions in pure water as a function of time after the application of voltage and as a function of distance from the surface of metallic electrodes have been found from theory by Morrow & McKenzie [11] by solving the continuity equations for hydronium and hydroxide ion concentrations simultaneously with Poisson’s equation for the electrostatic potential. In these calculations, no adsorption of ions was allowed nor any charge transport to or from the electrodes, the so-called ‘blocked electrode’ configuration. Solving these equations enabled the time dependence of the motion of ions in response to an applied electric field to be calculated. The field distribution in the steady state is reproduced in figure 8 and shows a symmetrical distribution of electric field intensity relative to the centre of the system. The field reaches 1.5 MV m^{-1} at the surface of both electrodes in water when the voltage between electrodes is 0.4 V and the electrode separation is $500 \mu\text{m}$.

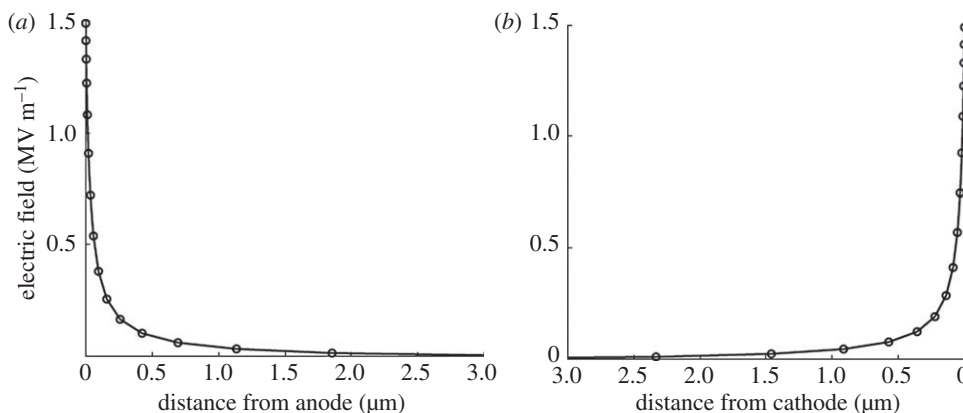


Figure 8. Calculated electric field as a function of distance from the electrode surface in pure water (a) near the anode and (b) near the cathode with a voltage of 0.4 V applied for 3 s. Reproduced with permission from Morrow & McKenzie.

The fields shown in [figure 8](#) are the result of the accumulation of ions near the electrodes. Some of the solvated hydronium ions may adsorb to the cathode surface, held there as a result of the screened image potential. In the vicinity of the anode, solvated hydroxide ions also accumulate in the double layer and some of these may adsorb to the surface. During the passage of current in the steady state, tunnelling electrons leaving the cathode, if they do not interact with an adsorbed ion, will be driven away by the electric field until they are finally scavenged by a hydronium ion. The repulsion of the electrons prevents space charge build-up so that the tunnelling probability of electrons at the electrodes is the rate-limiting process.

In order to interpret the findings of the previous section concerning the fraction of charge adsorbed to the electrode surface and the dimensions of the tunnelling barrier, some observations will now be made of the expected spatial distribution of potential experienced by an electron existing in its free state in water near a metallic electrode. First, the electrostatic potential energy of the electron in a water medium will be reduced from the value it would have in vacuum by the highly polarizable medium, the process known as ‘solvation’. The existence of solvated electrons in aqueous solution was postulated by Platzman [28] and they have been observed spectroscopically by Hart and Boag to have a lifetime of tens of microseconds [29]. Solvated electrons have binding energies relative to the vacuum at the surface of water of 1.6 eV and in the interior of water a binding energy of 3.3 eV [30,31].

Much of the literature on quantum mechanical tunnelling has been developed in connection with the behaviour of electrons at the surfaces of conductors and semiconductors in vacuum or at interfaces in the solid state, a field that has developed separately from that of quantum-oriented electrochemistry, where the application of quantum mechanical theory has been largely based on the work of Bockris & Khan, Gurney & Fowler, Marcus and Mott & Gurney [1,8,32,33]. There are several proposed models showing how an electron can be transferred from a metal to a hydronium ion [34–37]. Schematic diagrams of the potential barrier that is proposed to be present at the surface of an active electrode in aqueous solution, originating from the ideas of Gurney have been shown in published work by Bockris & Kahn [1], but the shape, height and width of the barriers were not stated.

(d) An update of the Gurney barrier scheme for tunnelling in electrolysis

The tunnelling of electrons through water following Gurney’s discussion of the quantum mechanics of electron tunnelling in electrolysis is illustrated in [figure 9](#), which shows the definition of some key energy differences on a re-creation of his potential energy scheme [7]. Gurney considered radiationless tunnelling transitions in this scheme. For example at the cathode,

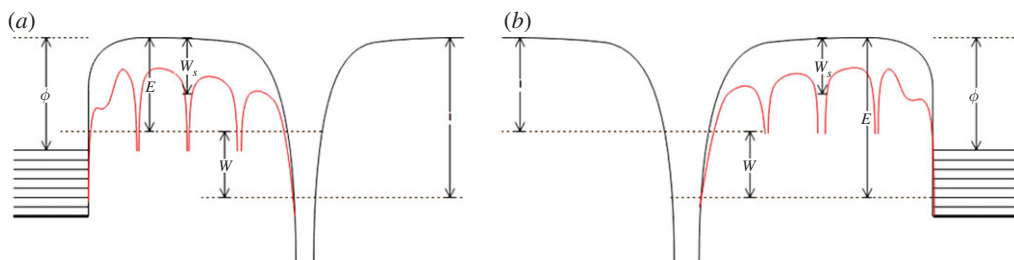


Figure 9. A re-creation of Gurney's original diagram of the electron potential energy distribution in water as a function of distance from a metallic electrode in the absence of an applied field. Intermediate states arising from electron-water interactions (in red) are added here to show their effect on lowering the tunnel barrier by an amount W_s . When voltage is applied, the tunnelling current is dependent on both the electron tunnelling current from the metal (cathode on the left (a)) to a positive ion vacant state and on the tunnelling of an electron from a negative ion state to the metal (anode on the right (b)). W is the ion hydration energy. ϕ is the work function of the metal. In (a) E is the neutralization energy of the solvated hydronium ion (energy released when an electron in vacuum is captured by a hydronium ion in solution). The hydration energy W is required to be supplied as the ion is neutralized. I is the ionization energy of the hydronium ion in vacuum (energy released when an electron in vacuum is captured by a hydronium ion in vacuum). These differ by the ion hydration energy W . In (b) I is the ionization energy of the hydroxide ion in vacuum (energy required to remove the electron from the ion in vacuum) and E is the neutralization energy of the solvated hydroxide ion (energy required to remove the electron from the hydroxide ion in water to the vacuum).

an electron tunnels from an initial occupied state in the metal electrode to an unoccupied electronic state of an ion in solution where the initial and final states have the same energy.

The hydronium and hydroxide energy levels are affected by solvation and are shifted with respect to the vacuum levels. The reason for the opposite effect of solvation on the energy shifts of the electron states of positive (hydronium) and negative (hydroxide) is readily understood as follows: for the positive hydronium ion, the solvation shell contains predominantly negative charge, raising the energy of the electron states relative to vacuum. The neutralization energy E is therefore smaller than the ionization energy I in vacuum by the solvation energy W . On the other hand, for the hydroxide ion, the solvation sphere is positively charged, so that solvation lowers the energy of the electron states with the result that the neutralization energy E in solution is larger than the ionization energy I in vacuum. These relationships are illustrated in figure 9. Solvation is also likely to extend the width of the barrier for tunnelling to or from the ion states to at least the nominal radius of the ion complex of associated water molecules [38,39].

Solvation also affects the work function of the metal electrodes. When an electron is taken from the Fermi energy in the metal to the water medium outside, an amount of work is done that is smaller than the work function, because the solvation of the electron lowers its energy relative to the vacuum. Since the solvation time of an electron in water is about several tenths of a femtosecond [40], comparable to the tunnelling time of an electron which is also in the femtosecond range (10 fs for one layer of water) [41], electrons enter the solvated state as they tunnel in much the same way as a photoexcited electron does [42]. The energy of the solvated electron is lowered by an amount W_s referred to as the vertical binding energy (VBE). The value for W_s has been found to lie in the range 3.03–3.27 eV [30,31,43]. The photoexcitation measurements of the work function of gold under water give the result 2.26 ± 0.10 eV [43]. This value is expected to be less than the work function in vacuum by the solvation energy of the electron, if the final state of the photoelectron is assumed to be solvated. Subtracting the work function under water from the work function in vacuum gives the result 2.82 eV, somewhat smaller than, but comparable to the solvation energy of the electron, confirming that the final state is solvated. The energy of a tunnelling solvated electron is represented in figure 9 by a spatially varying barrier with minima to indicate locally preferred binding configurations or intermediate

Table 3. Estimates of energy differences in the potential energy distribution for an electron undergoing transfer by tunnelling in the electrolysis of pure water, useful in quantifying the schematic of figure 9. Values for W are converted from tabulated molar energies of hydration.

quantity	energy (eV)	reference
Φ	5.1, 5.10–5.47	[43,48]
W_s	3.27 ± 0.10 , 3.3, 3.03 ± 0.3	[30,31,43]
I (hydronium)	5.25 (simulation)	[47]
I (hydroxide)	1.82 (affinity hydroxyl radical)	[45]
E (hydronium)	2.10 (simulation)	[47]
E (hydroxide)	9.2 (1.15 fwhm)	[44]
W (hydronium)	4.26	[49]
W (hydroxide)	4.38	[49]

states that represent the cavities in the water where the electron is relatively more strongly bound. These intermediate states will reduce the average barrier height.

The neutralization energy E for hydrated hydroxide ion was found to be large, having the value 9.2 eV (1.15 eV fwhm) measured spectroscopically [44], while the electron affinity of the free hydroxyl radical is small, having the value 1.83 eV [45], suggesting that the solvation energy of the hydroxide ion W is very large, of the order of 7 eV [46]. The apparent discrepancy may be due to the close association of hydroxide with its first hydrating water molecule to form a strongly hydrogen bonded cluster $H_3O_2^-$ so that the hydration studies of hydroxide in solution that give the lower value are actually referring to the additional hydration after the formation of this cluster.

In the case of solvation of the hydronium ion, there is less experimental observation than for hydroxide, but some simulation studies are available. The ionization potential in vacuum I , assumed equal to the electron affinity, is calculated for hydronium to be 5.25 eV and this decreases for solvation with 19 water molecules to 2.1 eV which can be taken as an estimate of E for hydronium [47]. Table 3 summarizes the available information concerning the barriers in figure 9 for electron tunnelling at the cathode and anode, including the work function of gold that lies in the range 5.1–5.4 eV [43,48].

The data of table 3 enable the Gurney schematic potential distribution to be placed on a quantitative basis. The barrier presented by the water to an electron tunnelling from the cathode in water should be less than the work function of gold under water (2.26 eV), since the tunnelling electron encounters the intermediate states. Gurney stated a condition on the energy of the initial (occupied) electron state relative to the energy of the final (unoccupied) state that must be satisfied in order to allow tunnelling in electrolysis to occur, namely that the initial electron state must be equal or higher in energy than the final state. In Gurney's opinion, the electron transfer would not occur until this condition is satisfied, by the application of voltage as necessary. A study of the best estimates of the energies (table 3) involved in electron transfer in figure 9 shows that Gurney's condition would prevent electrolysis at the low voltages where we observe current flow. For zero applied voltage, at the cathode, an upward transition from the metal Fermi energy at 5.1 eV below the vacuum to the solvated LUMO of the hydronium at 2.1–3.0 eV below the vacuum would be required. At the anode, an upward transition from the solvated HOMO of hydroxide at 9.2 eV below the vacuum to the Fermi energy of the cathode is required of around 4.1 eV would be required. The solvation energy W of both ions is above 4 eV and will be released during the electron transfer reaction. From the diagram in figure 9 it can be seen that in the absence of the solvation energy the reaction would be able to proceed at both electrodes at low voltages. Gurney's conditions for electron transfer are relaxed by Marcus theory [32], as noted by Santos *et al.* [6] in which fluctuations of solvent interactions occur that are linked to the fluctuations

in the electron probability distribution, enabling the solvation energy W for both hydroxide and hydronium to be stochastically reduced and allow the transitions to occur. The tunnelling process for electron transfer then takes place opportunistically. Further study of the fluctuations of the solvation energy will benefit from simulation approaches such as that of Otani *et al.* and Willard *et al.* [50,51].

A simple analytical expression can be obtained by setting up the problem as a tunnelling problem with multiple parallel pathways, each pathway being a one-dimensional tunnelling problem to or from an ion in solution. A related tunnelling model has been applied by Miyashita *et al.* [52] to describe tunnelling between two protein molecules separated by a water gap. The one-dimensional tunnelling probability will be expressed here in terms of the well known WKB approximation following the low-voltage tunnelling model of Simmons. We now seek to find the current density arising from the tunnelling from the metal to positive ions, considering this to be the rate-limiting step. We begin with a calculation of the number of electrons in the metal that are incident on the interface per unit area per unit time. The problem of finding the fraction of electrons per unit volume with velocity v_x in the x direction is a classic one in Fermi statistics and has the solution:

$$dN(v_x) = n(v_x)dv_x = \frac{4\pi m^2 kT}{nh^3} \ln \left\{ \exp \left[\frac{E_f - E_x}{kT} \right] + 1 \right\} dv_x, \quad (3.7)$$

where $E_x = (1/2)mv_x^2$ is the energy corresponding to the x component of velocity. The tunnelling current density is then the number of electrons incident on the interface per unit area per unit time, times the tunnelling probability of those electrons. In this model, at constant temperature, the number of incident electrons is constant so that the number of pathways, proportional to the number of ions available for tunnelling, times the tunnelling probability along each pathway gives the current as a function of applied voltage. The one-dimensional tunnelling probability is given by Simmons [24]:

$$J = \int_0^{v_m} v_x n(v_x) D(v_x) dv_x = \frac{1}{m} \int_0^{E_m} n(E_x) D(E_x) dE_x \quad (3.8)$$

$$= \frac{1}{m} \int_0^{E_m} \frac{4\pi m^2 kT}{nh^3} \ln \left\{ \exp \left[\frac{E_f - E_x}{kT} \right] + 1 \right\} \frac{\sqrt{\varphi_0}}{s} V \exp(-B_1 \sqrt{\varphi_0} s) dE_x, \quad (3.9)$$

where $D(v_x)$ is the tunnelling probability of the electron with velocity v_x , $D(E_x)$ is the corresponding probability for the same electron expressed in terms of E_x and v_m . E_m is the maximum energy of the electrons in the metal. We obtain the tunnelling probability as the product of two terms, equation (3.7) for the energy distribution and the WKB value for the probability of tunnelling through a rectangular barrier of height φ_0 and width s from the low-voltage result of Simmons. Now using the result of Morrow & McKenzie [11] for the voltage dependence of hydronium ions adjacent to the electrode we obtain:

$$\frac{1}{m} \frac{4\pi m^2 kT A_1}{nh^3} \frac{\sqrt{\varphi_0}}{s} V \exp(-B_1 \sqrt{\varphi_0} s) 10^{\alpha V - 7} \int_0^{E_m} \ln \left\{ \exp \left[\frac{E_f - E_x}{kT} \right] + 1 \right\} dE_x, \quad (3.10)$$

where A_1 , B_1 and α are adjustable parameters. Gathering all constants together, this relation has the simple functional form at constant temperature:

$$J = CV 10^{\alpha V - 7}, \quad (3.11)$$

where C is a constant. This equation provides a good fit to the data for pure water as shown in figure 2, giving a value of α of 4.07 lower than to the value 8.73 calculated by Morrow & McKenzie [11]. The case of the CO_2 -exposed water is more problematic as it contains electrolyte. The quantum mechanics based model of electron solvation in electrolyte by Lakhno and Vasil'ev describes how inertia polarization and Debye screening could contribute to an intensified localization of the solvated electron state, which in turn would lead to the electron solvation energy dependence on electrolyte concentration [53]. The effects of the additional anions in CO_2 -exposed water may explain why our data for this case are not well fitted by equation (3.11).

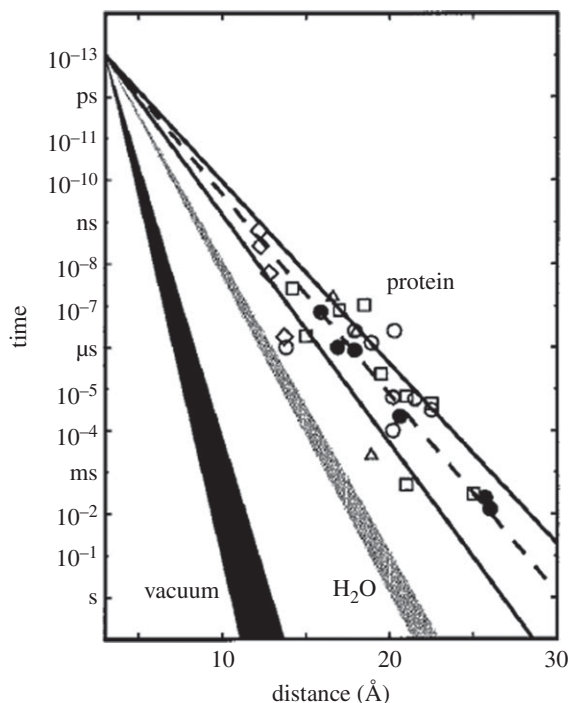


Figure 10. A schematic diagram reproduced from Ponce, Gray and Winkler [54] showing measurements of tunnelling time as a function of distance for electron transfer reactions within protein molecules, compared to tunnelling times in water and vacuum. The tunnelling times decrease and the tunnelling distances increase as the tunnelling medium changes from vacuum to water to protein molecules.

(e) Applications to biosensing

Our results are of practical significance as they suggest potential applications of electron tunnelling from an electrode into water for sensing molecular attachment at interfaces. The sensing of attachment of a probe molecule (protein or DNA for example) bound at the interface, to its complementary molecule is of importance in medical diagnosis. Figure 10 shows a schematic diagram taken from Ponce *et al.* [54] that illustrates the potential for the sensing of protein adsorption at an interface using the tunnelling current to and from the solution. Since the tunnelling time for electrons along protein molecules is faster than is expected through water, the presence of the molecules at the interface should strongly affect the tunnelling time and therefore the tunnelling current. Such a detection mechanism that uses tunnelling may have advantages of simplicity and speed over other proposed methods of molecular detection that rely on optical or plasmonic phenomena or semiconductor band bending at a conduction channel [55].

4. Conclusion

We have undertaken a study of the transient and steady-state currents drawn by gold electrodes immersed in pure water using small applied voltages in order to determine whether tunnelling between electrodes and ions in solution has a role in the electrolysis of water at low voltages. Our observations and analysis of the time dependence of the current that flows after switching voltage on or off confirms Gurney's early ideas and shows that some current is drawn by ions in solution and some by adsorbed ions. We have carried out an analysis of the steady-state current as a function of voltage and have derived two models for the tunnelling current that assumes the ion neutralization reactions take place by tunnelling of electrons between the electrodes and the

ions in solution. The agreement with observation provides further support for the contribution of tunnelling between electrodes and ions in solution. The first model assumes that the barrier at each electrode can be represented by an average tunnelling barrier and have used results obtained by Simmons for one-dimensional tunnelling to show the barrier for tunnelling at electrodes in water is wide and low, consistent with the presence of intermediate electron states in solution arising from electron solvation [24]. Literature measurements of the energetics of surface and bulk solvated states of an electron are used to add more detail to the schematic tunnelling potential barrier of Gurney. We find that tunnelling at the voltages we use would be prevented by the energetics as expressed by the original condition for electrolysis of Gurney. However, we propose that these conditions are relaxed by solvent fluctuations on the basis of the work of Marcus [32]. A model that assumes there are multiple one-dimensional parallel tunnelling pathways gives good agreement with the voltage dependence of the steady-state current for pure water, but not for CO₂-exposed water. In confirming the role of tunnelling at electrodes in water, our findings suggest applications of tunnelling in biosensing at interfaces in water.

Ethics. This work did not involve collection of data from any known life forms.

Data accessibility. All original data recordings are kept in a logbook exclusive for this work. The primary custodian D.R.M. should be contacted to arrange access to the logbook. E.G. has digitized and uploaded all the original and processed data openly accessible via the Microsoft OneDrive link: <https://1drv.ms/f/s!AkayW9lu7BO4hXlk00ir7CpnJ9ZG>.

Authors' contributions. E.G. and D.R.M. interpreted the results, wrote the paper. E.G. carried out the experiment, data collection and tunnel barrier calculation in consultation with D.R.M. D.R.M. implemented the idea of multiple pathways tunnelling model with E.G. fitting the model to the experimental data. All authors gave final approval for publication.

Competing interest. We have no competing interests.

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