



An improved approach for fabricating Ag/AgCl reference electrodes

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ABSTRACT

We report an improved approach for fabricating Ag/AgCl reference electrodes for use in Harned Cell measurements of pH. Standard fabrication procedures involve converting a proportion of Ag to AgCl. This is usually driven by applying a fixed current, instead the novel approach presented here uses a fixed potential. This has resulted in an ensemble of electrodes of superior repeatability. The transient current data provides an indication of the geometric surface area of each electrode, offering important information about the microstructure. This approach has far-reaching implications for improving the repeatability of Ag/AgCl electrodes and reducing uncertainty in pH measurement.

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1. Introduction

Sørensen introduced the concept of pH in 1909 [1]. Since then, measurements of pH have become increasingly widespread and have a major impact on our every day lives [2–5]. As pH measurement is universal, much research has been conducted to ensure measurement validity and traceability [6–8].

Primary pH values are determined using a “Harned cell” which is an electrochemical cell arrangement which does not contain a liquid junction and relies on well characterised Ag/AgCl reference electrodes for operation [9]. It has the potential to be a primary method for the absolute measurement of pH, providing that it can conform to the accepted definition of a primary method [10] that requires a methodology and operation that can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units. The performance of Ag/AgCl reference electrodes is of paramount importance for accurate pH measurement. A small change in the potential of a Ag/AgCl reference electrode makes a significant contribution to the measurement uncertainty. In metrological applications, excluding the determination of the molality of HCl used in the Harned cell, the reference potential of Ag/AgCl electrodes employed is the largest contribution to the measurement uncertainty of pH [9].

Thermal electrolytic Ag/AgCl reference electrodes are a conventional choice for Harned cell operation and have been studied extensively [11–13]. Recent work has shown that the

microstructure of the Ag/AgCl material has a large influence on electrode repeatability and performance [14,15]. A porous electrode presents a high efficiency surface, enabling high exchange current densities at equilibrium, thereby resulting in a highly reproducible and stable reference potential. However, electrodes with a high degree of porosity suffer from an increased probability of creating a mixed potential as deeper solution penetration may allow contact of the electrolyte with the Pt wire skeleton supporting the Ag/AgCl. Impurities may also be attracted to the Pt/Ag interface during annealing as a result of it being a high free energy surface [16]. Therefore it is important to understand how to control the electrode microstructure to optimise performance.

National metrology institutes (NMIs) maintaining primary standards for pH measurement, prepare thermal electrolytic Ag/AgCl electrodes in-house. [17–20] Electrodes are usually prepared from Ag₂O paste which is reduced to Ag by thermal conversion in a furnace at around 500 °C. Electrolytic conversion is then used to convert typically 10–25% of the Ag to AgCl by making the electrode the anode in an electrochemical cell with a 0.1 M HCl electrolyte. Anodisation is usually performed by applying a fixed current (often 1 mA) for a pre-determined time period to provide the required charge, calculated from the mass of deposited Ag using Faraday's Law. During the process, Ag undergoes an anodic oxidation to AgCl, at the surface exposed to the electrolyte, and forms an AgCl layer. The geometric surface area of the Ag sphere can be vastly different from one electrode to another as this parameter has been shown to be very sensitive to differences in preparation procedure [16]. Hence when anodising using constant current, the current density applied to each electrode varies considerably. Furthermore recent work by Stoica et al. [21] revealed an “s” shape profile for the

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potential transient of several Ag/AgCl electrodes during anodisation at constant current. This was attributed to complete coverage of the electrode surface with AgCl. In this case, as a layer of resistive AgCl formed, a steep rise in potential was observed in order to maintain constant current. As the thickness of the AgCl layer increased, it became increasingly more difficult for the solution to penetrate the material, and hence the potential progressed towards a plateau. The transient potential plots revealed for several electrodes that an elevated potential was applied for the majority of the process. This is likely to stress the electrode and impact on performance. In addition this process will lead to fast AgCl growth on the outside of the sphere such that it actually promotes the formation of a “blocking” layer of AgCl. A process operated at constant current results in a different current density applied to each electrode that is dependent on available geometric surface area. Hence this may be detrimental to the repeatability of electrodes produced and therefore a major issue in regard of the stringent selection criterion employed for Harned cell use (typically individual reference electrodes which differ from the average of the group by more than 100 mV are rejected [22]).

We report, for the first time, a new approach for anodising Ag/AgCl electrodes for use in the Harned Cell. The method involves applying a constant potential slightly above the open circuit potential (OCP) of the electrode, rather than at constant current, for the duration of the anodisation process. This self-limiting “softer” approach ensures that as the resistive AgCl layer builds up on the electrode surface, the current is reduced, thereby slowing down the rate of formation, thus not forcing the process and blocking solution penetration to the deeper electrode. This should mitigate any possible damage caused by subjecting the electrode to large potentials for prolonged periods of time. A further benefit is that the rate of formation of AgCl between electrodes is independent of the geometric surface area as the current is limited by the unconverted Ag. This approach also provides an indication of the geometric surface area of each electrode which offers important information about the microstructure. Measurements of electrodes prepared using this procedure demonstrate a considerable improvement in repeatability compared to those prepared at constant current. This is a significant step towards developing an optimum methodology for Ag/AgCl electrode fabrication for use in the Harned cell.

2. Experimental

Thermal electrolytic Ag/AgCl reference electrodes were prepared by thermal decomposition (100 °C for 1 h followed by 500 °C for 2 h) of three separate applications of Ag₂O paste to a Pt wire (99.99%, 0.5 mm diameter). Prior to electrode preparation, the Ag and Pt wires were immersed in concentrated nitric acid to remove surface contaminants. Wires were then rinsed thoroughly with distilled water.

Approximately 15% of the material was electrolytically converted to AgCl in a solution of 0.1 mol dm⁻³ HCl. The amount of Ag on each electrode was determined prior to anodisation and the charge required to convert 15% to AgCl was calculated. A three-electrode cell was employed in which the potential between the working electrode (the Ag/AgCl electrode under test) and the counter electrode (platinum flag) was controlled relative to a commercial Ag/AgCl reference electrode (double junction reference, Fisherbrand). Electrodes were anodised using a Potentiostat (N-stat, Ivium Technologies) in either constant current (chronopotentiometry) or constant potential (chronoamperometry) mode. In constant current mode, the cell was fixed to pass a current of 1 mA at the working electrodes. In constant potential mode, the potential

between the working electrodes was fixed at 50 mV above the OCP of each individual electrode.

All solutions were prepared using 18.2 MΩ cm distilled and deionised water (MilliQ, Millipore) and ultra high purity chemicals (Fisher, UK). All experiments were carried out with solution temperatures of 20 ± 2 °C in a temperature controlled laboratory. All solutions were degassed with nitrogen before use (metrology grade, BOC UK). A positive pressure of nitrogen was maintained over the solution during experimentation.

Measurements to investigate the potential difference between Ag/AgCl reference electrodes were carried out by using one of the thermal electrolytic Ag/AgCl electrodes as a de-facto reference and placing it in a 0.01 mol dm⁻³ HCl solution with the other Ag/AgCl electrodes and allowing a period of at least twelve hours for equilibrium to be reached. All of the potentials are reported with respect to this de-facto reference electrode. The potential difference between the electrodes and the reference was measured as a function of time using a high accuracy Keithley 2001 multimeter. Measurements were taken every 30 s and were acquired using in-house software written in LabVIEW 8.6.

Electrochemical impedance spectroscopy (EIS) measurements used the same three electrode configuration as for anodisation. These measurements were carried out at open circuit potential using a potentiostat with an integrated impedance analyser (N-stat, Ivium Technologies). The measurements were carried out in 0.01 mol dm⁻³ HCl solution, with a signal amplitude of 10 mV across a frequency range of 100 kHz to 0.1 Hz with 10 points per decade.

Scanning electron microscopy (SEM) measurements were made with a MX2500 thermionic emission scanning electron microscope (Camscan) fitted with an INCA Energy⁺ Si/Li energy-dispersive X-ray (EDX) spectrometer (Oxford Instruments) for chemical microanalysis. Secondary electron signals, backscattered electron signals and characteristic X-rays were detected using an Everhart-Thornley detector, a four quadrant solid-state Si detector and a liquid nitrogen cooled Si/Li detector respectively. Secondary and backscattered electron images were recorded at an SEM accelerating voltage of 20 kV. The secondary electron images show surface topography and the backscattered electron images show variation in atomic number contrast across the field of view. Elemental distribution maps were obtained using an accelerating voltage of 20 kV, a working distance of 35 mm and final aperture of 70 μm.

3. Results and discussion

The transient potential exhibited by a Ag/AgCl electrode during anodisation provides important information on physico-chemical processes occurring. Electron microscopy has been previously used to study thermal electrolytic Ag/AgCl electrodes [23]. Fig. 1 shows an EDX image with elemental analysis of the cross section of a Ag/AgCl electrode anodised in 0.1 mol dm⁻³ HCl solution under a constant current of 1 mA. The images confirm the formation of AgCl on the outer layers of the Ag sphere which may explain the presence of an “s” shaped potential transient during anodisation. The images show that the AgCl produced does not penetrate further than about a quarter of the distance from the surface to the Pt wire. It is known that 10–25% of the Ag should be converted to AgCl to produce electrodes with good repeatability and stability [24]. However the implications of an uneven distribution of AgCl within the sphere of material are not known. The images in Fig. 1 show electrodes with a composition of AgCl much greater than 15% at the surface and with little or no AgCl towards the centre. The performance of this distribution compared to an homogenous arrangement of Ag and AgCl would be an interesting future study. We can hypothesise that this electrode may be less stable than one

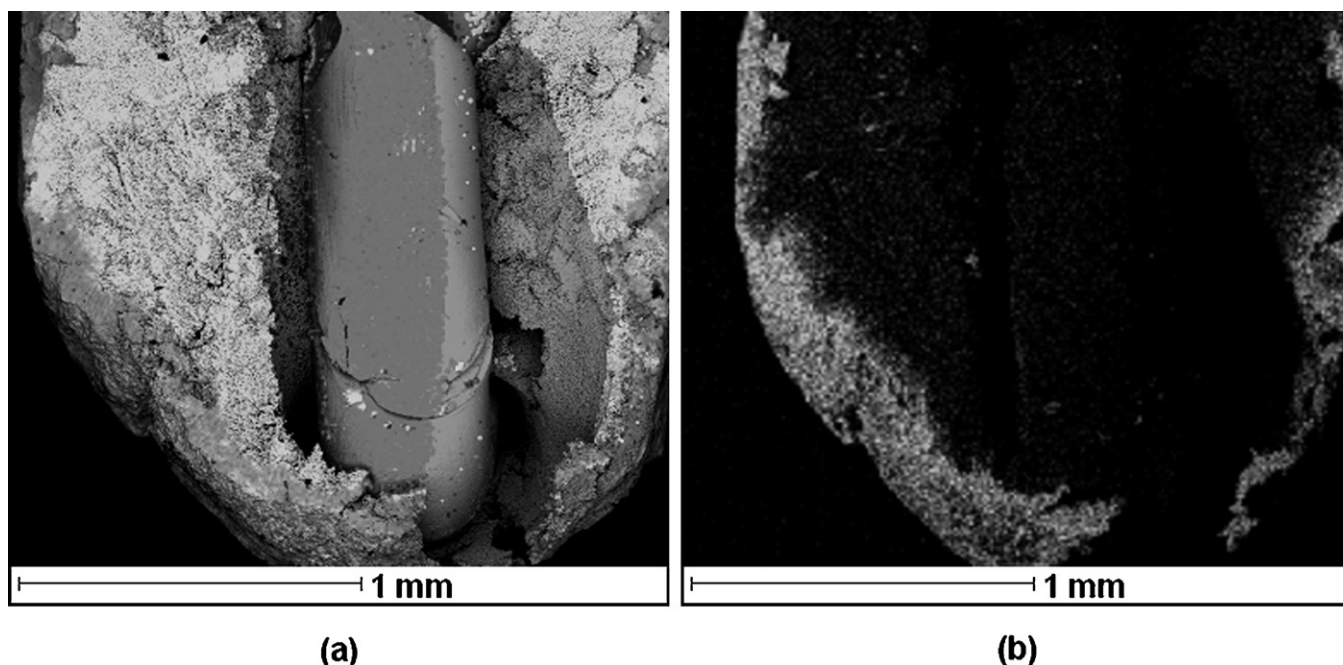


Fig. 1. EDX images showing the elemental analysis of the cross section of a Ag/AgCl electrode after anodisation at a constant current of 1 mA. (a) Cl containing layer on the outside (darker shading) compared to the elemental Ag (lighter shading). The contrast is exaggerated in (b) with an image of just the chloride analysis (light pixels).

where the Ag/AgCl is evenly distributed, since it may be more difficult for an electrochemical couple with high exchange current density to be established.

Fig. 2(a) shows transient potential data versus surface area for anodisation of six pieces of Ag wire of variable length (4 mm, 11 mm, 18 mm, 25 mm, 32 mm and 39 mm). A constant current of 1 mA was used and hence a different current density was applied to each wire. The s-shape profile exhibited for each can be assigned to the process of AgCl formation, with the sudden rise in potential resulting from complete coverage of the surface. As expected, the time to the inflection point of each wire occurs in the order of available surface area of Ag, starting with the 4 mm wire at 12 s. It is also informative to observe the gradient of the transient prior to

the inflection point as this provides an indication of the rate of formation of AgCl and thus is an indicator of current density. Fig. 2(b) shows the time of the inflection point and the initial gradient for each transient as a function of surface area. With fixed current, an increase in surface area will result in a decrease in current density and hence a decrease in the rate of formation of AgCl. As expected, when the surface area is increased, the time of the inflection point increases while the initial gradient of the transient decreases. An explanation for the deviation from linearity may be attributable to a physical or chemical process which is accelerated at higher current densities and occurs at the surface of the Ag sphere. A process such as a change in the porosity of the Ag/AgCl material during anodisation would result in a change in the available Ag for conversion to AgCl and hence bring about a change in the inflection

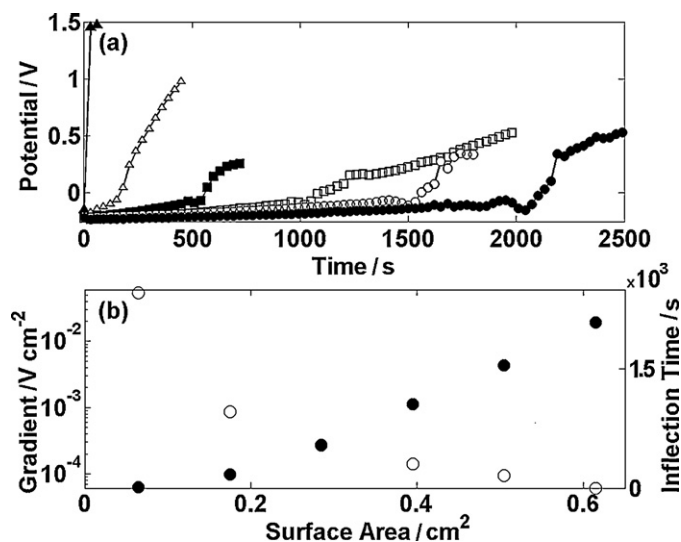


Fig. 2. Potential vs. commercial Ag/AgCl reference as a function of time measured during the anodisation process at constant current. (a) Potential transient for Ag wires of different surface area. (b) Gradient of the transient prior to the inflection point (open circles and left axis) and the time of the inflection point (filled circles and right axis) vs. surface area of the wire.

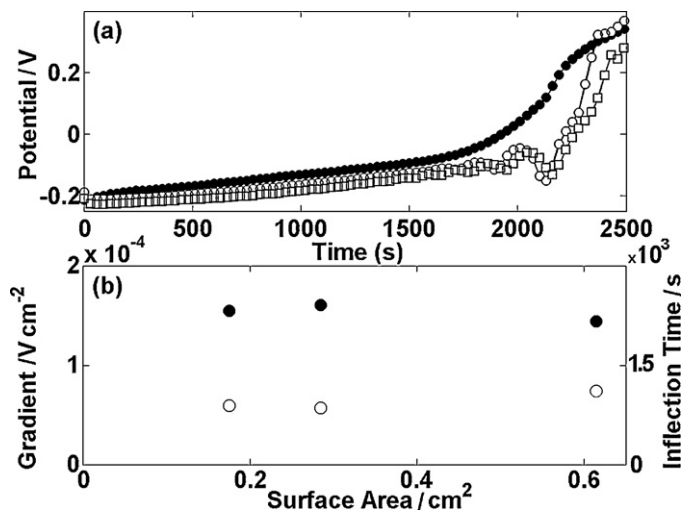


Fig. 3. Potential vs. commercial Ag/AgCl reference measured during the anodisation process at constant current density. (a) Potential transient for Ag wires of different surface area. (b) Gradient of the transient prior to the inflection point (open circles and left axis) and the time of the inflection point (filled circles and right axis) vs. surface area of the wire.

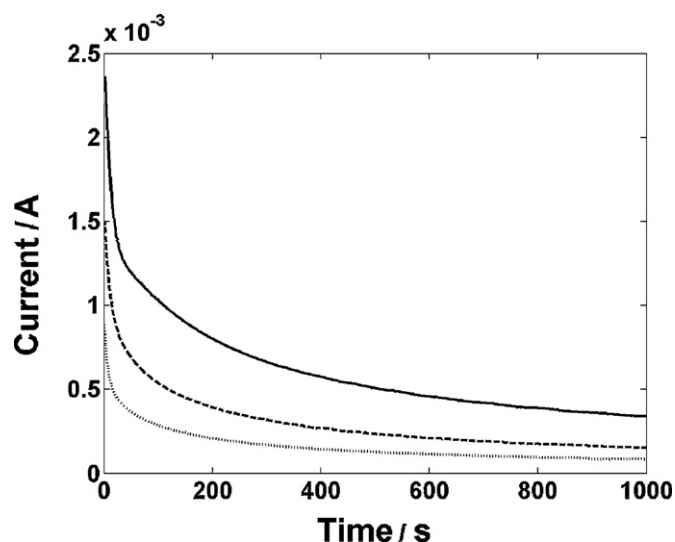


Fig. 4. Current vs. commercial Ag/AgCl reference measured during the anodisation process at constant potential for Ag wires with different surface area. In each case the potential was set at 50 mV above the open circuit potential.

point and rate of AgCl formation. The deviation from linearity in Fig. 2(b) might also result if higher current densities brought about a reduction in available Ag for conversion to AgCl thereby reducing the inflection point and increasing the initial gradient. This effect would be larger at lower surface areas and become negligible for Ag wires with larger surface areas.

Fig. 3(a) shows the potential transient during anodisation of three pieces of Ag wire at a constant current density of 1 mA cm^{-2} (prescribed in a standard procedure) [18]. The profile is similar for each with a similar formation of AgCl (shown by the inflection points and initial gradients in Fig. 3(b)). This demonstrates that if the surface area of the Ag is known, it is possible to apply a constant current density ensuring the same rate of AgCl formation and an ensemble of electrodes with better repeatability than prepared at constant current. However due to the porous “sponge like” nature of Ag/AgCl electrodes it is difficult to determine the geometric surface area. In most cases the applied current during anodisation is determined from the mass of the Ag deposited on the Pt wire rather than the geometric surface area, resulting in a different current density applied to each electrode. This effect as well as the high applied potentials evident in Figs. 2(a) and 3(a) are likely to affect the repeatability and performance of the ensemble.

Applying a constant potential above the OCP of each electrode during anodisation, instead of a constant current, should allow the rate of AgCl formation to be similar for each electrode and independent of the available surface area. During this process the current will decay to zero when the available Ag has been converted to AgCl and will ensure that the electrode is not subjected to high damaging potentials. Fig. 4 shows the current transients for anodisation of three pieces of Ag wire (5, 10 and 20 mm) at a fixed potential of 50 mV above OCP. Preliminary measurements (data not reported here) showed that the optimum anodisation potential is around 50 mV. A lower potential was insufficient to drive the conversion of Ag to AgCl, and a larger potential may be more damaging to the electrode. In each case a charge was applied so that 15% of Ag on each electrode was converted to AgCl. Each transient exhibits almost identical gradients in the initial linear regime and similar current profiles. The standard deviation of the gradients in the first 15 s of data is 0.016 mA s^{-1} . These results indicate that a similar current density has been applied to each electrode as a similar rate of formation of AgCl occurs. Differences between equilibrium and starting current (when a layer of AgCl has formed) of 0.83 mA, 1.4 mA and

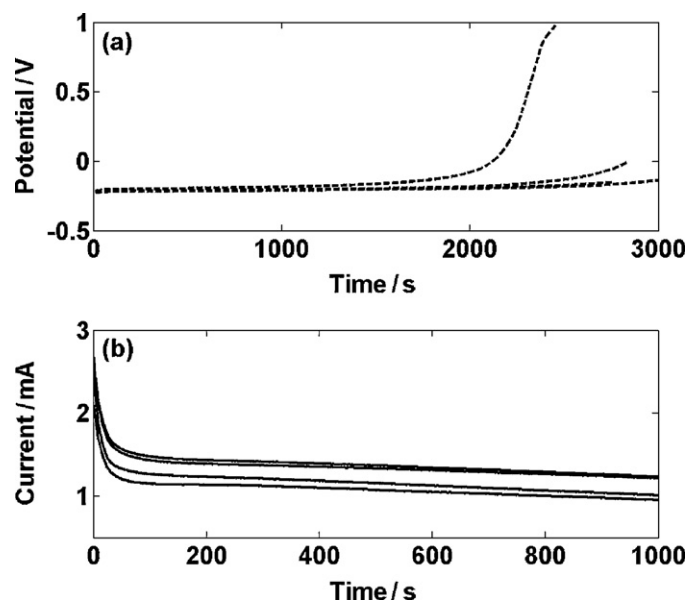


Fig. 5. Transient signatures of several Ag/AgCl electrodes vs. a commercial Ag/AgCl reference measured during the anodisation process at (a) constant current (10 mA) and (b) constant potential (50 mV above OCP). The geometric surface area of each electrode was similar.

2.2 mA were determined from Fig. 4 for wires of length 5, 10 and 20 mm respectively. An almost linear relationship between these parameters is observed.

Fig. 5(a) and (b) shows the transient potential and current profiles for Ag/AgCl electrodes anodised under constant current and constant potential respectively. In Fig. 5(a), a constant current of 1 mA was applied and an anodisation time was calculated to ensure that 15% of the Ag on each electrode was converted to AgCl (determined from deposited mass of Ag). Each anodisation signature stops at a different stage in the s-profile showing the variability of this procedure as a result of using mass of Ag to determine anodisation time as opposed to geometric surface area. Contrary to this Fig. 5(b) shows almost identical signatures under constant potential. The initial gradients for the first 15 s are almost identical with a

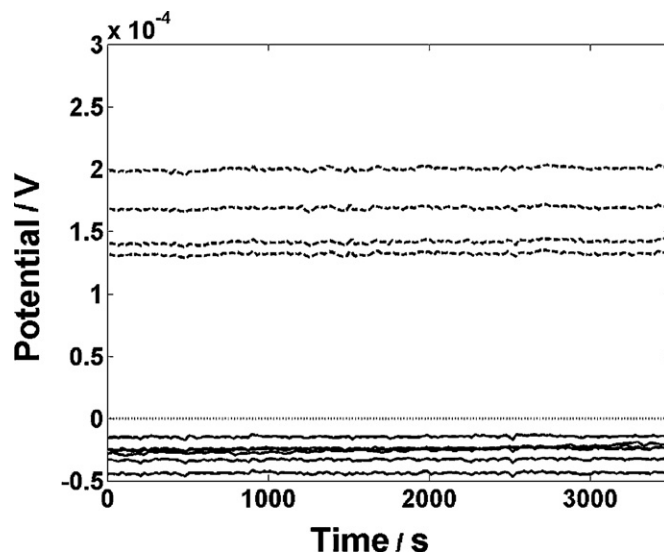


Fig. 6. Potential vs. Ag/AgCl defacto reference prepared using an anodisation process at constant potential. Electrodes anodised using constant potential and constant current are shown with solid and dashed lines respectively. The geometric surface area of each electrode was similar.

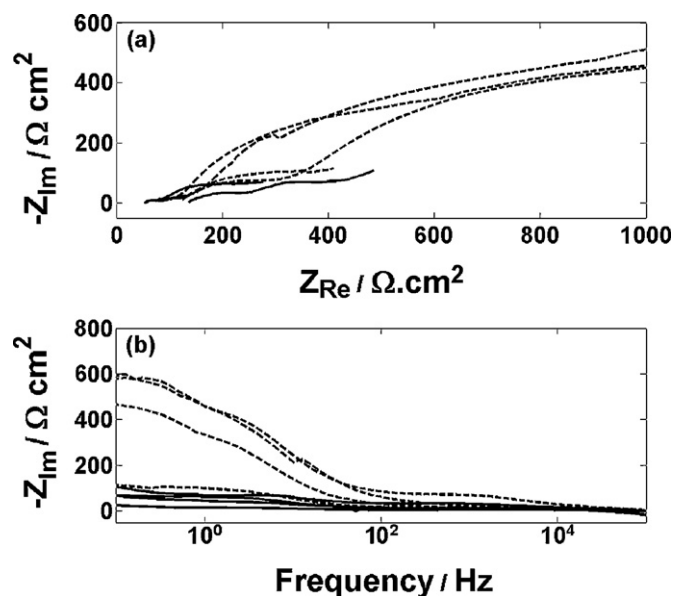


Fig. 7. Impedance spectra of electrodes shown in Fig. 5. (a) Complex plane (Nyquist) representation of the impedance between 100 kHz and 0.1 Hz, obtained at open circuit potential. (b) Imaginary part of impedance as a function of frequency. Electrodes anodised with constant potential and constant current are represented with solid lines and dashed lines respectively. The geometric surface area of each electrode was similar.

standard deviation of only 0.006 mA s^{-1} for the ensemble of 4 electrodes. This demonstrates that similar anodisation conditions can be provided without knowledge of the geometric surface area of each electrode. Differences between equilibrium and starting current of 1.51 mA, 1.79 mA, 1.86 mA and 1.94 mA were determined from Fig. 5 (b) for the four Ag/AgCl electrodes. The mean of these values is 1.78 mA. The difference between equilibrium and starting current for the three Ag wires presented in Fig. 4 was plotted against respective surface area (not shown). A linear least-squares fit was

used to determine a mean geometric surface area of 0.24 cm^2 for the four electrodes presented in Fig. 5(b). Assuming the Ag/AgCl structure can be modelled as a sphere and the electrolyte has negligible penetration, an average area of 0.24 cm^2 implies a Ag/AgCl sphere with a radius of 0.14 cm. This compares closely to average measurements made using vernier callipers and confirms that this method is suitable for semi-quantitative measurement of geometric surface area.

Fig. 6 presents the potential of the Ag/Ag electrodes prepared using constant current (dashed lines) and constant potential (solid lines) respectively versus a defacto Ag/AgCl reference. A difference of $189 \mu\text{V}$ exists between the mean of each ensemble of electrodes prepared following the different anodisation methods. The difference in the absolute potential between the two ensembles may confirm the presence of a change in stoichiometry from AgCl when the reaction is forced under constant current. The electrodes prepared at constant potential are shown to be considerably more repeatable with a standard deviation of the equilibrium potential of $9 \mu\text{V}$ compared to $31 \mu\text{V}$ for those prepared using a fixed current. For measurements of pH using the Harned cell, it is the repeatability of the AgCl electrodes rather than the absolute potential that is of importance as measurements between cells with different electrodes impact directly on the measurement uncertainty. Therefore this result confirms the virtue of using the constant potential procedure for preparing Ag/AgCl electrodes for pH measurement.

Electrical impedance measurements have been used to interrogate our findings and probe the processes taking place during the two different anodisation procedures. Measurements of the same electrodes presented in Figs. 5 and 6 were made and are shown in Fig. 7 where dotted and solid lines represent electrodes anodised under constant current and constant potential respectively. In these measurements, the distance between the counter and reference electrodes to the electrode under test were kept constant to minimise spectral artefacts and allow for a quantitative interpretation of the spectra. Fig. 7(a) presents the complex plane representations (Nyquist diagram), $-Z_{Im}$ vs. Z_{Re} at different frequencies, where Z_{Im} is the imaginary component and Z_{Re} is the real component of

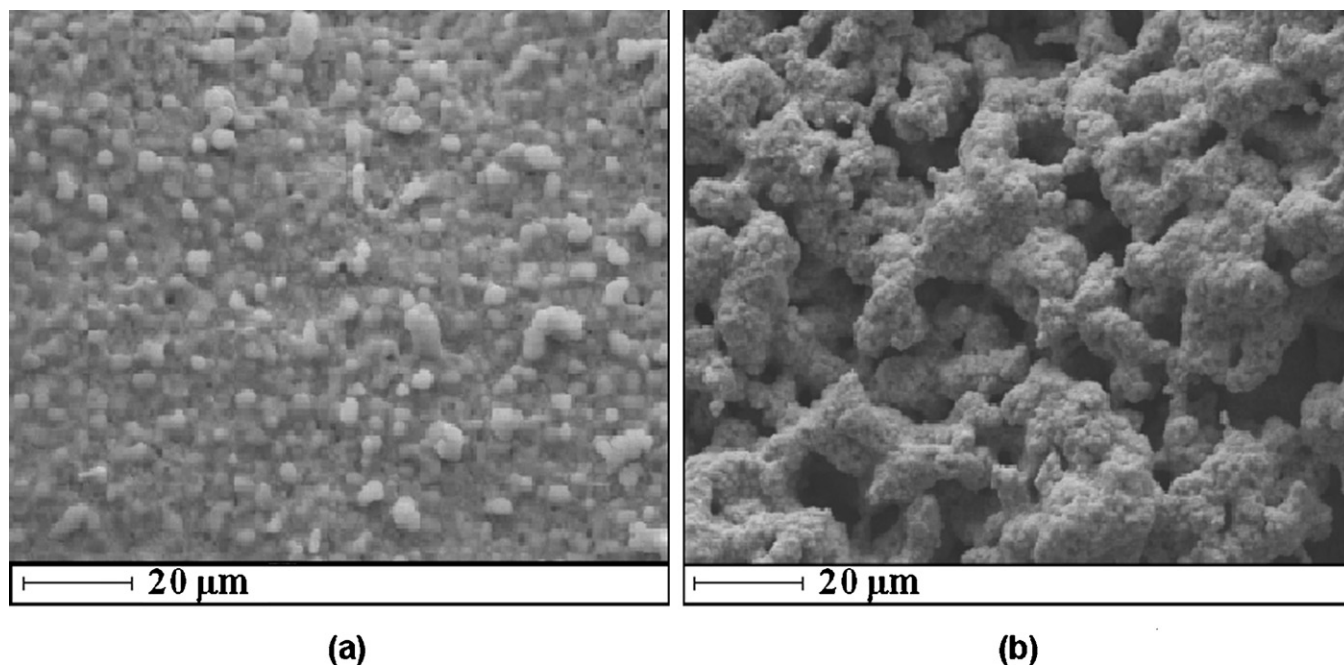


Fig. 8. Exemplar SEM images of a Ag/AgCl electrode after anodisation at (a) constant current and (b) constant potential.

the complex impedance. The spectra have been normalised to the geometric area of each electrode. The plots of the Ag/AgCl electrodes anodised under constant current exhibit much larger values of $-Z_{lm}$ vs. Z_{Re} compared to those prepared under constant potential. Electrodes prepared using constant potential reveal a slightly curved line at low frequencies which is characteristic of a diffusion processes taking place. Both of these observations are consistent with a difference in structure in the Ag/AgCl material as a result of the different anodisation processes undertaken. The data in Fig. 7(a) suggests a more porous structure for electrodes anodised using constant potential.

Fig. 7(b) shows the imaginary part of complex impedance plotted against frequency and confirms the findings in Fig. 7(a). The data shows a larger value of Z_{lm} for the Ag/AgCl electrodes anodised under constant current which is consistent with a denser structure. The frequency at which Z_{lm} exhibits a maximum value corresponds to the relaxation frequency related to the relaxation time of mobile charges. A subtle shift of the relaxation frequency towards higher values is observed for electrodes made under constant potential (solid lines). This is due to a decrease in the relaxation time and indicates a faster movement of the charges, consistent with a more porous structure. The average Z_{lm} maximum for electrodes prepared under constant current is approximately 0.1 Hz compared to 1 Hz for those prepared under constant potential. This is in agreement with previous findings [21].

The impedance response of the electrodes has been modelled using the Randles equivalent circuit. However, because of the porosity of the electrodes, a constant phase element (CPE) has replaced the double layer capacitance [25]. The empirical CPE impedance function, Z_{CPE} , is expressed according to [26]:

$$Z_{CPE} = Z_0(j\omega)^{-\alpha} \quad (1)$$

where Z_0 is a constant, j is the imaginary number and ω is the angular frequency ($\omega = 2\pi f$ and f is the frequency). The exponent α is a dimensionless parameter, describing the CPE behaviour. For an ideal capacitor with a smooth surface, α is equal to 1.

Fig. 8 shows SEM images of Ag/AgCl electrodes prepared by (a) constant current and (b) constant potential anodisation procedures. The images reveal a more porous structure for electrodes anodised at constant potential and are in accordance with the electrical impedance measurements. This suggests that the current density applied to an electrode has an effect on the microstructure. A higher current density shows a tendency to reduce the porosity of the Ag/AgCl material. This supports the claims for the deviation from non-linearity in Fig. 2(b).

4. Conclusions

We have investigated a new approach for anodising Ag/AgCl electrodes by applying a constant potential above the OCP which is self-calibrating as it takes account of existing impurities when setting the anodisation potential. Unlike the conventional constant current method, this provides a self-limiting approach ensuring

that the rate of AgCl formation is independent of the available surface area of Ag and is therefore constant for each electrode produced. During anodisation, the current decays to zero when the available Ag has been converted and the electrode is not subjected to high damaging potentials. This has resulted in electrodes of superior repeatability and increased conductivity due to the different microstructure. The transient current data collected during anodisation also provides a measure of the geometric surface area of the Ag/AgCl electrode, providing important information on the microstructure. This work has far-reaching implications for reducing uncertainty in pH measurement and in emerging areas in the field [27], and the new method is preferred as an improvement on existing techniques.

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