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# Influence of fabrication procedure on the electrochemical performance of Ag/AgCl reference electrodes

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# ABSTRACT

The influence of several parameters in the preparation procedure of thermal–electrolytic Ag/AgCl electrodes on the resulting electrode performance has been studied. In particular, we report the effect on electrode performance of subtle variations in the preparation of silver oxide paste used for electrode manufacture, in thermal annealing conditions employed and in the procedure for electrochemically converting a fraction of the electrode from silver to silver chloride. Scanning electron microscopy and electrochemical impedance spectroscopy have been used to study the characteristics of the electrodes produced. This work reveals a correlation between the electrochemical behaviour and surface physical characteristics – in particular electrode porosity. The outputs of this study have positive implications for improving the accuracy and comparability of primary pH measurement.

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# 1. Introduction

The procedure for primary pH measurement is based on a potentiometric cell, commonly referred to as a Harned cell. The cell is designed in order to avoid any liquid junction. This is the only system accepted by International Union of Pure and Applied Chemistry (IUPAC) and the Bureau International des Poids et Measures (BIPM) for primary pH measurements. The primary potentiometric pH determination is based on the measurement of the difference in potential between a hydrogen-ion-sensing platinum-hydrogen electrode and a Ag/AgCl reference electrode in a buffer solution under test. Chloride ions at known concentrations are added to this buffer solution to enable the potential difference at zero chloride concentration to be obtained by extrapolation. The relationship used for pH calculation is given in Eq. (1).

$$pH = -\log(a_H^s) = \lim_{m_{Cl} \to 0} \left\{ \left( \frac{E^{\text{measured}} - E^0}{RT/F \ln(10)} \right) + \log(m_{Cl}) \right\} + \log(\gamma_{Cl}^0)$$
(1)

where  $a_H^s$  is the activity of hydrogen ions in the solvent,  $E^{\text{measured}}$  is the measured potential (corrected to 1 atm partial pressure of hydrogen),  $E^0$  is the standard potential of reference electrode, R is the molar gas constant, T is the temperature, F is the Faraday

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constant,  $\gamma_{Cl}^0$  is the activity coefficient of chloride ions and  $m_{Cl}$  is the molality of chloride added to the solvent.

Ag/AgCl reference electrodes are frequently used in electrochemistry as they possess numerous beneficial characteristics such as electrochemical reversibility, high exchange current, low polarization (when passing small currents) and highly reproducible potential. The final characteristic is the main reason [1] why the liquid-junction free Ag/AgCl electrodes are used as reference electrodes for primary pH measurements. These electrodes are generally only produced by National Metrology Institutes (NMIs) as they require meticulous fabrication procedures and specific expertise. The current market is too small for commercial production.

For primary pH measurements the typical expanded uncertainty is usually no more than 0.005 pH [2]. Generally, the contribution of the standard potential ( $E^0$ ) of the Ag/AgCl electrode is about half of the final estimated uncertainty [3,4], and electrodes agreeing within 60–100 µV should be used in order to meet the target uncertainty. The standard potential is an intrinsic characteristic of a reference electrode. According to the IUPAC recommendations, the determination of the standard potential should be made in an aqueous 0.01 molal HCl solution [5]. The 1978 IUPAC report invokes a maximum inaccuracy on  $E^0$  values of about 0.2 mV using the generic preparation methods suggested.

Ag/AgCl electrodes may be grouped into three types, according to the preparation method [6]. Provided that a suitably optimised protocol is followed, all electrode types exhibit good precision, accuracy and reliability, with bias potentials within the confidence interval required for primary standard measurements. It is essential that the same electrode type is used both in the determination of

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 $E^0$  and in the parallel emf measurement of the IUPAC-prescribed Harned cell [5]. This study investigates the thermal–electrolytic type as it has been used more extensively than any other [7–9].

Brewer and Brown [10] have shown that microstructure plays an important role in electrode performance. The porosity of the electrode is one of the most important aspects of its microstructure. A porous electrode presents a high efficiency surface enabling high exchange current densities at equilibrium, thereby resulting in a highly reproducible reference potential. However, a high degree of porosity also increases the 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. Moreover, impurities may also be attracted to this Pt/Ag interface during annealing as a result of it being a high free energy surface [11]. This may have a significant and variable impact on the potential exhibited by the electrodes and should be avoided if possible. Therefore to achieve highly repeatable Ag/AgCl electrodes it is imperative to control their degree of porosity. A number of parameters in the preparation of Ag/AgCl electrodes are believed to influence the porosity [1]. These parameters include the purity of materials used for the Ag<sub>2</sub>O paste preparation (presence of impurities such as bromide have a detrimental effect), the efficiency of the washing process carried out to remove ionic impurities from the Ag<sub>2</sub>O paste, the storage solutions used and the conditions employed for converting Ag<sub>2</sub>O to Ag.

It therefore seems plausible that the electrode microstructure and hence electrode performance can be controlled by manipulating certain parameters in the preparation procedure. We demonstrate for the first time, the influence of several key parameters in the electrode preparation procedure (Ag<sub>2</sub>O paste, thermal decomposition conditions and anodisation) on the porosity characteristics of the electrodes produced. This work is a significant step towards developing an optimum methodology for making reproducible Ag/AgCl electrodes.

# 2. Experimental

Two electrode preparation methods, in use at the Laboratoire National de Métrologie et d'Essais (LNE) and the National Physical Laboratory (NPL) have been studied. The preparation of thermal–electrolytic electrodes involves three main stages, detailed in Fig. 1: (i) synthesis of Ag<sub>2</sub>O paste, (ii) thermal decomposition of Ag<sub>2</sub>O to form metallic Ag (thermal annealing) and (iii) conversion of Ag to AgCl by anodisation.

To assist later discussion of the data, L1 and N1 are used to represent protocols employed for the production of Ag<sub>2</sub>O paste at LNE and NPL respectively. L2 and N2 represent protocols employed for thermal annealing and anodisation at LNE and NPL, respectively.

#### 2.1. Electrode fabrication

#### 2.1.1. Preparation of Ag<sub>2</sub>O paste

AgNO<sub>3</sub> and NaOH (Sigma Aldrich, 99.9999% and 99.998%, respectively) were used for the synthesis of Ag<sub>2</sub>O. In order to obtain homogeneous Ag<sub>2</sub>O crystals in the desired size range (0.1-15 microns) [12] a solution of NaOH with a concentration of 5 M for L1, and 1 M for N1, was added dropwise to a vigorously stirred AgNO<sub>3</sub> solution. Since nitrate anions are more easily removed from the Ag<sub>2</sub>O precipitate by a washing process than hydroxide ions, nitrate anions were kept in excess during the reaction. Ag<sub>2</sub>O paste produced using method L1 was aged for 1 month during which time it dried out and became substantially more viscous, whereas paste produced using N1 was used immediately after preparation.

#### 2.1.2. Thermal annealing

Successive layers of Ag<sub>2</sub>O were applied in order to obtain a sphere of material on the platinum wire (99.999%, Goodfellow, UK). This sphere was then annealed in order to obtain Ag. Complete thermal decomposition of the Ag<sub>2</sub>O to Ag and O<sub>2</sub> occurs at 400 °C [13]. Both procedures used temperatures in excess of this value. For L2, each electrode was annealed for 15 min at 450 °C. For N2, electrodes were heated for 30 min at 100 °C (in order to first remove water from the Ag<sub>2</sub>O paste) and then at 500 °C for 2 h.

#### 2.1.3. Anodisation

The anodisation process used a three-electrode cell in which the potential of the working electrode (WE–the Ag/AgCl electrode under test) was controlled relative to a pseudo-reference electrode (RE – platinum flag). During the electrolysis, the current through the cell was kept constant using a Potentiostat (Keithley Model 228A for L2 and EGG Princeton Applied Research Model 263A for N2). A current was passed between the WE and the counter electrode (CE – also a platinum flag). Approximately 15% of the Ag was converted to AgCl using L2 and N2 respectively. In the process, Ag undergoes an anodic oxidation to AgCl, at the surface exposed to the electrolyte, and forms an AgCl layer. The process took place in aqueous HCl solution (1 M for L2 and 0.1 M for N2). For L2, the current was fixed at 10 mA, the anodisation time being calculated for each electrode individually, according to the total mass of Ag in each electrode, by using Faraday's law (constant current electrolysis):

$$Q = I \cdot t = n \cdot F \tag{2}$$

where Q is the total electric charge passed through the electrolyte, I is the current applied, t is the duration of the electrochemical process, n is the amount of Ag converted to AgCl and F is the Faraday constant. For N2, Eq. (2) was used to calculate the applied current required for a fixed anodisation time of one hour.

# 2.2. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements used the same three electrode configuration. These measurements were carried out at open circuit potential at different frequencies using a potentiostat with an integrated impedance analyser (N-stat, Ivium Technologies). The measurements were carried out in 0.01 M HCl solution under potentiostatic control, with a signal amplitude of 10 mV. The frequency was varied from 100 kHz to 0.1 Hz with 10 points per decade.

### 2.3. Scanning electron microscopy

Scanning electron microscopy (SEM) measurements were made with a field-emission scanning electron microscope (FE-SEM), Carl-Zeiss-Supra 40. An accelerating voltage of 10 kV was used with a working distance of 3.7 mm and a final lens aperture of size 30 mm. Secondary electron images were acquired using an in-lens detector.

# 3. Results and discussion

#### 3.1. Potential measurements during the anodisation process

The evolution of the potential during electrode anodisation provides a useful tool to interpret the physico-chemical processes occurring. Typically the final anodisation voltage is greater than the initial value. This is due to the formation of AgCl, which is a substantially non-conductive substance, resulting in an increase in resistance. The effective conductivity of such a layer depends on the electrode porosity, as this influences the available surface area and the degree to which the electrolyte is able to penetrate through



Fig. 1. Preparation steps for thermal-electrolytic Ag/AgCl electrodes. The steps involved in L1 and L2 can been seen on the left-hand and those involved in N1 and N2 on the right-hand side. L2 involves 7 successive layers of Ag<sub>2</sub>O whereas N2 only 3 layers.

the non-conductive silver chloride layer and maintain contact with the conductive silver underneath the surface.

Fig. 2 shows the potential during the anodisation process for several Ag/AgCl electrodes prepared by the two institutes. The final voltage of Ag/AgCl electrodes prepared at LNE (Fig. 2a) is smaller than those prepared at NPL (Fig. 2b). Moreover, the variation in anodisation voltage with time of electrodes prepared at each institute is vastly different, suggesting a contrast in electrode porosity and AgCl distribution. The slightly upwardly curving profile in Fig. 2a suggests that the AgCl formed has not fully covered the available surface area by the end of the anodisation procedure. This indicates the presence of a larger surface area for the LNE electrodes compared to those prepared by NPL (Fig. 2b) and hence a more porous structure. The S-shape profile in Fig. 2b is characteristic of a less porous electrode with a lower available surface area. The sudden rise in potential being attributed to the complete coverage

a 0.4 Potential/V 0.3 0 5 10 15 20 25 30 b 2.0 Potential/V 1.0 0 0 10 20 30 40 50 60 Time / min

**Fig. 2.** Evolution of the potential vs. Pt (pseudo-ref) during the anodisation process for several Ag/AgCl electrodes using (a) L1–L2 and (b) N1–N2.



These findings are important as P. Brewer et al. [14] previously showed that the porosity of Ag/AgCl electrodes is a parameter that requires careful control to ensure good electrode comparability. Since the anodisation is the last step in the preparation, it is not clear which process (Ag<sub>2</sub>O paste preparation, thermal conversion or anodisation) has the largest influence on the electrode microstructure. Therefore we have investigated the influence of all these parameters on the electrode porosity.

The influence of protocols L2 and N2 on the transient anodisation potential of electrodes prepared from  $Ag_2O$  paste from methods L1 and N1 is shown in Fig. 3a and b respectively. In Fig. 3a, different signatures are observed when the thermal annealing and



**Fig. 3.** Variation of the potential vs. Pt (pseudo-ref) measured during the anodisation process. (a) Shows electrodes prepared from  $Ag_2O$  paste using L1 with protocols L2 (filled triangles) and N2 at different viscosities (open triangles and filled squares). (b) Shows the same with  $Ag_2O$  paste prepared using N1 with protocols L2 (open circles) and N2 with different  $Ag_2O$  paste aging times (open squares and filled circles).

anodisation protocol (L2 and N2) is changed. Protocol L2 results in a featureless transient, whereas N2 produces the 'S' shape profile obtained in Fig. 2b. This suggests that changes in the thermal conversion and anodisation processes alter the porosity of the final structure of electrodes prepared from Ag<sub>2</sub>O paste using method L1. In Fig. 3b, the 'S' shape profile is obtained for each of different protocols (L2 and N2) employed. This suggests that Ag<sub>2</sub>O paste prepared using method N1 will result in a structure with low porosity regardless of the thermal conversion and anodisation procedures employed.

Fig. 3a shows two profiles from electrodes prepared with Ag<sub>2</sub>O paste at different viscosities (open triangles–less viscous and filled squares-more viscous). The data suggests that a more viscous Ag<sub>2</sub>O paste produces an electrode with a more porous structure. Fig. 3b shows two profiles from electrodes prepared from Ag<sub>2</sub>O with different aging times (filled circles and open squares) However the similar profiles suggests no influence of the Ag<sub>2</sub>O paste age on the porosity.

Mendizza et al. [15] suggested that the conductivity of the deposited AgCl layer increases with increasing acidity in the solution. Based on the previous conclusions, the increased conductivity of L2 electrodes cannot be exclusively explained by the acidity of HCl solution. As Fig. 3 shows, the concentration of the HCl solution acts mainly to influence the kinetics of AgCl formation: faster AgCl formation occurs with more concentrated HCl solutions.

Fig. 4 shows SEM measurements of the surface morphology of some representative electrodes. The images confirm the previous observations. Fig. 4a shows a porous structure for electrodes prepared by method L1–L2. In contrast, a dense structure is shown in Fig. 4c for electrodes prepared by method N1–N2. A structure with intermediate porosity is shown for an electrode prepared with the Ag<sub>2</sub>O paste protocol from one institute (L1) and the thermal conversion and anodisation protocols from another (N2).

Therefore we may hypothesise that the electrodes obtained using L1 and L2 are characterized by a porous but inhomogeneous AgCl layer, with several regions having different AgCl content (Fig. 4a). This is likely to result in poor electrochemical performance. Despite some controversy over the mechanism by which the AgCl film nucleates and grows on an anodized Ag surface, there are some sources [16] that state that the concentration of the HCl electrolyte may affect the loss of AgCl from the deposited layer during the anodisation process. According to the well-known common-ion effect, the solubility of AgCl will decrease with an increase of chloride concentration in the electrolyte. Thus, in order to limit the loss of AgCl from the deposited layer into the solution and also to prevent the formation of AgCl<sub>2</sub><sup>-</sup>, an HCl solution at or below 1 M should be used [15]. Since this condition is met by the protocols studied, the poor homogeneity of the AgCl layer in Fig. 4a could be related to the nature of the anodisation process: i.e. using a fixed anodisation time and a less concentrated electrolyte (N2) may produce a more homogeneous layer of AgCl (Fig. 4b and c). However, further work is required to investigate this.

Further SEM was carried out to study the effect of different thermal annealing protocols (L2 and N2) on the microstructure of electrodes fabricated from  $Ag_2O$  paste prepared using L1.

Fig. 5a shows the image of an electrode prepared with annealing protocol L2. The microstructure is considerably less homogeneous than when annealing protocol N2 is used (Fig. 5b). In this case the pores have a similar size of around 10  $\mu$ m. The difference between these structures can partially be explained with the fact that the intermediate step in N2, which consists of annealing each electrode for 30 min at 100 °C, allows for the removal of water molecules from the Ag<sub>2</sub>O paste before increasing the temperature to 500 °C. A quick and violent loss of water by annealing in one step may create larger and more variable pores (as is the case with L2).

### Table 1

Parameters determined by using complex impedance spectroscopy.

Electrode type	Porosity factor <sup>a</sup>	Relaxation frequency (Hz)	α	$D_s$
L1-L2 L1-N2	14 3	501.2 501.2	0.24 0.41	5.2 3.4
N1-L2	1.2	316.2	0.34	3.9
N1-N2	1	158.5	0.60	2.7

<sup>a</sup> The porosity factor =  $R_{p2-P2}^{\Omega}/R_{iectrode}^{\Omega}$ , where  $R_{\chi}^{\Omega}$  is the ohmic resistance of electrode X,  $\alpha$  is related to constant phase element behaviour (a value of 1 indicating a perfect capacitor), and  $D_s$  is the fractal nature of the electrode.

Hence we may conclude that the water content of the  $Ag_2O$  paste and its subsequent removal during annealing has an affect on the porosity of the final electrode. It seems that the lower the water content in the initial paste, the more porous the resulting electrode. This may be a result of a porous structure already beginning to form as the paste dries. The hydrated paste will not allow a pore structure to form prior to annealing. Furthermore the more extreme the annealing conditions the more rapid the removal of the water during annealing and hence the more extensive the pore structure created by this process: leading to more porous electrodes. These conclusions support the SEM data.

### 3.2. Electrochemical impedance spectroscopy

EIS measurements were performed to validate our earlier conclusions and further investigate the influence of the Ag<sub>2</sub>O paste, thermal annealing conditions and anodisation protocol on the microstructure of the resulting Ag/AgCl reference electrodes. Variables such as the distance between the CE and RE to the electrode under test have been kept constant in order to minimise any artefacts in the data and allow for a quantitative interpretation of the spectra.

The complex plane representations (Nyquist diagrams), displaying –  $Z_{lm}$  vs.  $Z_{Re}$  for different values of frequency, are shown in Fig. 6, where  $Z_{lm}$  is the imaginary component and  $Z_{Re}$  is the real component of the complex impedance. The spectra have been normalised to the geometric area of the electrode. Three distinct regions can be identified. Firstly the partial contribution of electrolyte and cell configuration at high frequencies (the frequency range is too limited to reveal the entire arc). Secondly a semicircle at intermediate frequencies when the system is under kinetic control, as a result of an electrochemical charge transfer step at the electrode–electrolyte interface. Lastly a straight, or slightly curved, line at low frequencies which is characteristic of diffusion processes.

Since all the electrodes have been analyzed in the same HCl solution, the shift of their respective ohmic resistance is due to the difference in the active surface (real area), and thus is related to the porosity. As the SEM images have shown (Fig. 4), the least porous electrode structure is produced from N1–N2 and is shown in Fig. 6d. The absence of a significant diffusion process is consistent with its dense structure. The ratio between its ohmic resistance and those of each of the other electrodes enables a determination of the relative porosity factor, indicating how many times the electrodes are more porous than those produced using N1–N2. The porosity factor calculated for electrodes in Fig. 6 is given in Table 1.

Fig. 7 shows the imaginary part of complex impedance versus frequency, corresponding to the data displayed in Fig. 6. The data shows an increase in magnitude of  $Z_{lm}$  with a decrease in porosity of the electrode. The frequency at which  $Z_{lm}$  exhibits a maximum value corresponds to the relaxation frequency related to the relaxation time of mobile charges. The shift of the relaxation frequency towards higher values, observed for electrodes made from Ag<sub>2</sub>O paste with L1 (Fig. 7a), is a consequence of the decrease in the relaxation time and indicates a faster movement of the charges, coherent with a more porous structure associated with these electrodes.



Fig. 4. SEM images of Ag/AgCl electrodes after anodisation: (a) L1–L2, (b) L1–N2, (c) N1–N2. In (a), region 2 has twice as much AgCl content as region 1.



Fig. 5. SEM images of electrodes made from Ag<sub>2</sub>O prepared using L1. Images (a) and (b) were obtained before anodisation and correspond to annealing procedures L2 and N2, respectively.

Due to their porosity, the systems cannot be modelled using the idealized circuit elements. Thus, the use of distributed impedance elements such as a constant phase element (CPE) are required [17]. The empirical CPE impedance function, Z<sub>CPE</sub>, is expressed according to [18]:

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

where  $Z_0$  is a constant, j is the imaginary number and  $\omega$  is the angular frequency ( $\omega = 2\pi f$  and f is the frequency). The exponent  $\alpha$  is a dimensionless parameter, describing the CPE behaviour. For an ideal capacitor with a smooth surface,  $\alpha$  is equal to 1. This parameter also expresses the deviation from an ideal system and can be quantified by plotting the imaginary part of the impedance,  $Z_{lm}$ , as a function of frequency using a logarithmic scale (Fig. 8) [19].



Fig. 6. Complex plane (Nyquist) representation of the impedance obtained at open circuit potential. (a), (b), (c) and (d) Represent electrodes prepared using L1–L2, L1–N2, N1–L2 and N1–N2, respectively, between 100 kHz and 0.1 Hz.



**Fig. 7.** Imaginary part of impedance as a function of frequency. (a) shows electrodes prepared from Ag<sub>2</sub>O paste using L1 with open triangles and open squares representing protocols L2 and N2, respectively. (b) Shows electrodes prepared from Ag<sub>2</sub>O paste using N1 with filled triangles and filled squares representing protocols L2 and N2, respectively.

As the imaginary part of impedance is independent of the electrolyte resistance, the slope is constant in the whole frequency range.  $\alpha$  will then be equal to the negative slope. The values of  $\alpha$ , determined in the frequency domain from 10<sup>4.5</sup> to 10<sup>3.3</sup>, are given in Table 1.

The exponent  $\alpha$  may also be related to the fractal dimension of the surface,  $D_s$ , by [20]:

$$\alpha = \frac{1}{D_{\rm s} - 1} \tag{4}$$

The smaller  $\alpha$ , the higher  $D_s$ , corresponding to an electrode with a greater fractal character. The porosity as well as the microstructural defects observed on the surface of the dense electrodes could be considered as a form of fractal geometry. A slightly higher  $D_s$  value but a smaller porosity factor obtained for N1–L2 compared to L1–N2 electrode could be explained by the presence of macroscopic cracks on the electrode surface of the latter.

Hence we may conclude that impedance spectroscopy is a very powerful method by which to characterise the Ag/AgCl electrodes. The most useful parameters to measure are: the exponent defining how far the capacitive element in the equivalent circuit deviates from that of an ideal capacitor, and the real component of



**Fig. 8.** Imaginary part of the impedance as a function of the frequency (logarithmic scale). Open triangles, open squares, filled triangles and filled squares represent electrodes prepared using L1–L2, L1–N2, N1–L2 and N1–N2, respectively. The slope for each plot was determined using data between 10<sup>3.3</sup> and 10<sup>4.5</sup> Hz.



**Fig. 9.** Voltage stability at equilibrium of investigated Ag/AgCl electrodes. Open triangles, open squares, filled triangles and filled squares represent electrodes prepared using L1–L2, L1–N2, N1–L2 and N1–N2, respectively. The measurements were carried out in 0.01 molal HCl solution, under a nitrogen atmosphere, at room temperature. A thermal electrolytic Ag/AgCl electrode was used as a *defacto* reference. Each point represents a mean value of the potential over a 3 h measurement period.

impedance. It has been shown that the larger the deviation from an ideal capacitor, the more porous the electrode. Equally the larger the real component of impedance at a given frequency, the less porous the electrode. The results have confirmed previous observations made in Section 3.1 that the wetter the initial Ag<sub>2</sub>O paste, and the less violent the removal of the water during annealing, the denser and less porous the electrodes produced.

# 3.3. Relative voltage measurements

The value of the standard potential ( $E^0$ ) depends, among other things, on the quality of the Ag/AgCl interface with the electrolyte. Experience shows that the main contribution, about 50%, of the overall pH uncertainty is contributed by the  $E^0$ . In order to reach an overall expanded uncertainty for primary pH measurements of less than 0.005 pH, it is necessary to reduce the contribution from  $E^0$ . The use of electrodes with similar morphology should therefore minimise the dispersion of the  $E^0$  values, improving the final accuracy and minimising uncertainty.

The performance of the Ag/AgCl reference electrodes fabricated with the different Ag<sub>2</sub>O paste, annealing and anodizing protocols has also been studied by evaluating the stability of their potential at equilibrium in 0.01 M HCl solution with respect to a *defacto* Ag/AgCl reference. This method is commonly used for electrode selection prior to Harned cell measurements of pH. Selection is based on the dispersion of the individual voltage compared to the average value of the group. The selection criteria is specific to each NMI, however, in order to meet uncertainty requirements, the usual acceptable range for measured electrode potentials is about <100  $\mu$ V [21]. In this analysis we will consider the mean potential of the group of electrodes rather than just looking at the difference between the highest and lowest result. The results of the potential measurements are presented in Fig. 9, each point representing the mean value over a 3 h measurement period.

The majority of electrodes satisfy the criterion employed for pH measurements (most deviate <100  $\mu$ V from the reference electrode). As this approach uses another Ag/AgCl electrode from the same batch as a *defacto* reference, it allows for a comparison between the electrodes.

The mean potential difference of L1-L2 and L1-N2 electrodes to the reference is vastly different which further confirms the sensitivity of Ag<sub>2</sub>O paste prepared using L1 to the annealing and anodising protocols employed. This corroborates the findings in Fig. 3a. Electrodes made from  $Ag_2O$  paste prepared using N1 are shown to be much less sensitive to the annealing and anodisation protocols (L2 and N2), with both N1–L2 and N1–N2 exhibiting very similar equilibrium voltages. This again supports the results in Fig. 3b where the profile of the anodisation transient was unchanged when a different annealing or anodisation protocol was employed.

The difference in mean potentials between the four electrode types could be explained by a difference in porosity, which will affect the amount of AgCl formed and the access of the electrolyte to impurities within the body of the electrode, and supporting Pt wire [12]. Electrodes prepared using N1–N2 and N1–L2 show a similar difference in potential to the reference. From earlier results their porosity is expected to be similar. Electrodes prepared using L1–N2 show a shift in mean potential to the reference. This can be explained by a change in porosity (Fig. 4b) which shows a more porous structure compared to electrodes prepared using L1–L2 (Fig. 4a). Electrodes prepared using L1–L2 show an even larger shift in mean potential to the reference and an even more porous structure (Fig. 4c).

We may conclude that the absolute voltage characteristics of Ag/AgCl electrodes produced are difficult to assess because of the correlation with the voltage reference electrode used. Therefore the salient criterion (apart from electrode slope which has not been assessed here) is the relative positions of their mean voltages. This gives some indication of the effect of each method on relative equilibrium potential – which is often a surrogate indication of other parameters such as porosity. This supports previous observations that the drier L1 paste produces more porous electrodes, and seems much more sensitive to the annealing and anodisation protocol as compared to the wetter N1 paste which produces less porous electrodes and seems to be much less sensitive to the annealing and anodisation regime used.

# 4. Conclusions

The accuracy of primary potentiometric results depends on the structural characteristics of Ag/AgCl reference electrodes. For achieving reliable pH measurements, some of the Ag/AgCl reference electrode properties need to be well controlled. This task is very difficult since many parameters have been identified as influencing the final electrode characteristics. In this context, the present work has advanced the understanding of the influence of electrode preparation technique on electrode morphology, especially its porosity.

The role of the microstructure in affecting the behaviour and response of the electrodes has been investigated, i.e. during anodisation and prior to their use in the Harned cell. The present work highlights the interest of using non-destructive electrochemical methods for the evaluation of the electrode porosity. The complex impedance spectroscopy appears to be an excellent investigative tool, also allowing comparison of porosity with fractal geometry.

Further research should be carried out to study further the relationship between porosity and electrode performance. Organizing an international comparison on this topic could be a possible way to gain a better understanding of the effect of different electrode preparation protocols on electrode performance. This would have positive implications for pH measurements and may impact on the use of Ag/AgCl electrodes in emerging new areas of electrochemical research [22].

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