Demonstration of the micro-porous structure of silver/silver chloride electrodes and the implications for Harned Cell operation

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Richard J. C. Brown
Martin J. T. Milton

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National Physical Laboratory
Queens Road, Teddington, Middlesex, TW11 0LW

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Executive Summary

The stability of silver/silver chloride reference electrodes when moved between different electrolyte solutions is limited by the small amount of solution transferred. The time required for the Ag/AgCl electrode potential to stabilise has been shown to increase with electrode size in an empirical fashion. The results presented in this report suggest the presence of a micro-porous structure in the electrodes that limits the rate at which traces of any previous solutions are diluted by any new solution environment. Operational implications for the stability and accuracy of the Harned Cell used as the primary standard for pH measurements and the certification of primary reference buffers are discussed[‡].

[‡] Presented to the CCQM Electrochemical Analysis Working Group, Paris, April 2004.

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1. Introduction

The measurement of pH [1] is an extremely important and commonly undertaken physico-chemical determination [2, 3]. It is also generally agreed that the determination of pH is the most frequently performed measurement in analytical science and process chemistry [4, 5], therefore ensuring the validity and traceability of pH measurements [6,7] is of the utmost importance.

Primary pH standard values are determined from an electrochemical cell arrangement without transference known as the “Harned cell” [1] which relies on well-characterised Ag/AgCl reference electrodes for its operation. The Harned cell 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 [8] 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 stability of the potential of silver/silver chloride reference electrodes when moved between different electrolytes is known to be of importance during Harned Cell operation but the effect has never been fully investigated. This phenomenon was first commented upon by R. G. Bates in the 1940s and has recently been re-investigated by K. W. Pratt [9]. It is common practice for Ag/AgCl electrodes to be stored in 0.01M HCl solutions when not in use and then transferred to Harned cells containing HCl or buffer solutions (with added chloride) for measurements to be performed. An initial, often large, change can be observed in the reference potential of the Ag/AgCl reference electrode when moved between solutions (as compared to a stabilised Ag/AgCl electrode in the new solution). This potential then decays away as the electrode equilibrates to its solution environment as any trace of the previous solution diffuses out of the pore structure of the Ag/AgCl electrode and the new solution diffuses in. Such shifts in the electrode potential can have significant implications for the accurate operation of the Harned Cell and the throughput of the certification of primary reference buffers. This paper investigates, for the first time, the timescale of the equilibration process and crucially the effect of electrode size on the equilibration time. These results suggest the presence of a micro-porous structure in the electrodes that limits the rate at which traces of any previous solutions are diluted by any new solution environment.

2. Experimental

The Ag/AgCl reference electrodes were of the thermal-electrolytic type made according to literature procedures [2,10,11]. These procedures result in an electrode consisting of a sphere of a porous nature, comprised of Ag (approximately 80% mole fraction) and AgCl (approximately 20% mole fraction), at the end of a silver wire. Several electrodes were made with different masses resulting in different sizes of spheres. The average diameter of the electrode spheres was determined from a minimum of sixteen equally spaced measurements using Vernier callipers around each of the three orthogonal axes of the sphere. The uncertainty in this value was characterised by the standard deviation of the mean. Typically the electrodes varied in diameter between 2 and 5 mm.

All solutions were prepared gravimetrically 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^{o}C using a water bath when necessary. All solutions were degassed with argon (99.9999%, BOC, UK) before use. A positive pressure of inert gas was maintained above the solution during experimentation.

One of the Ag/AgCl electrodes was placed in a solution of 0.025 M Na_2HPO_4 / 0.025 M KH_2PO_4 and was chosen as a *de facto* reference for the results presented here. All potentials are quoted with respect to this. All other Ag/AgCl reference electrodes were placed in a 0.01 M HCl solution and allowed to equilibrate overnight. The electrodes were removed from the HCl solution, excess solution was carefully removed with laboratory cloth, and placed in a phosphate buffer solution with the ‘reference’ Ag/AgCl reference electrode. The potential difference between the two electrodes was then measured as a function of time with a high-accuracy Keithley 2001 Mulitmeter. Measurements were taken every 20 seconds and acquired on a PC using Labview software. In a separate experiment one Ag/AgCl electrode was first equilibrated in a solution of 0.025 M Na_2HPO_4 / 0.025 M KH_2PO_4 and then the potential transient measured as described above. All experiments were repeated at least 5 times on different days to ensure the repeatability and reproducibility of the data.

3. Results and Discussion

Figure 1 shows selected potential transients measured for 7 different sizes of Ag/AgCl reference electrode. These potential plots have been offset to ensure that the final equilibrium potential measured between the 'reference' and test electrodes was zero. Potential differences at equilibrium, caused by phenomena such as mechanical stress or impurities in the electrode [12], are common in these electrodes, but were only in the range 5-75 μV before correction. It can be seen that the initial potential differences are very large and decay with time. The larger the electrode, the greater the timescale for equilibration to occur. At least one hour is required for most of the electrodes to equilibrate satisfactorily, with the largest ones needing more than two hours.

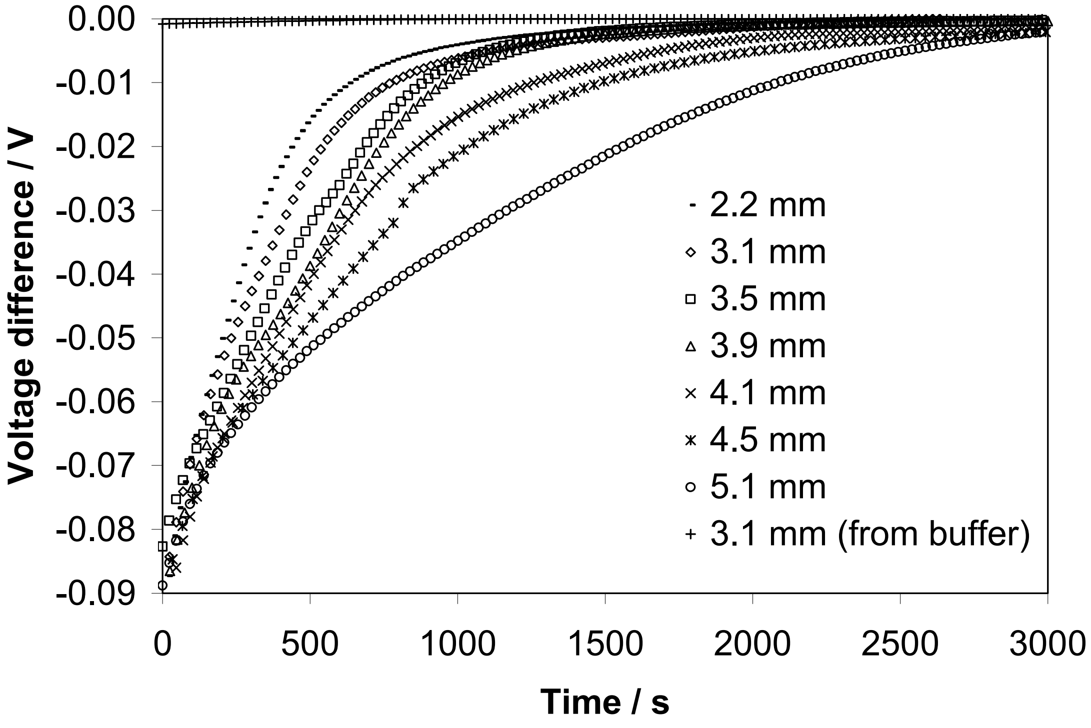

Figure 1. Selected transient potential difference measurements for Ag/AgCl electrodes of varying size equilibrated in HCl and then transferred to a phosphate buffer solution. One electrode [3.1 mm (from buffer)] was equilibrated in phosphate buffer solution before transfer.

The electrode that had been equilibrated in a separate phosphate buffer solution showed a very small initial potential difference and equilibrated to within 60 μV in 5 mins. This result suggests the value of electrode pre-conditioning in a similar solution to the one that the electrode is about to be used in as a method to avoid large potential transients and instability in Harned Cell operation. Pre-conditioning also helps to avoid contamination in the Harned Cell from other electrolytes which the Ag/AgCl electrodes have been standing in before transfer.

It can be seen that there is a strong correlation between the size of the electrode and the rate of decay. The observed decay with time was fitted to a first-order exponential function of the type $y = Ae^{-kt}$ (using OriginPro 7 graphical software) where t is the elapsed time in seconds, y is the measured voltage in volts and A is the measured voltage when $t = 0$. The results of this analysis are plotted in Figure 2, which shows that there is a very strong correlation between the rate of decay of the measured potential difference and the diameter of the Ag/AgCl electrode.

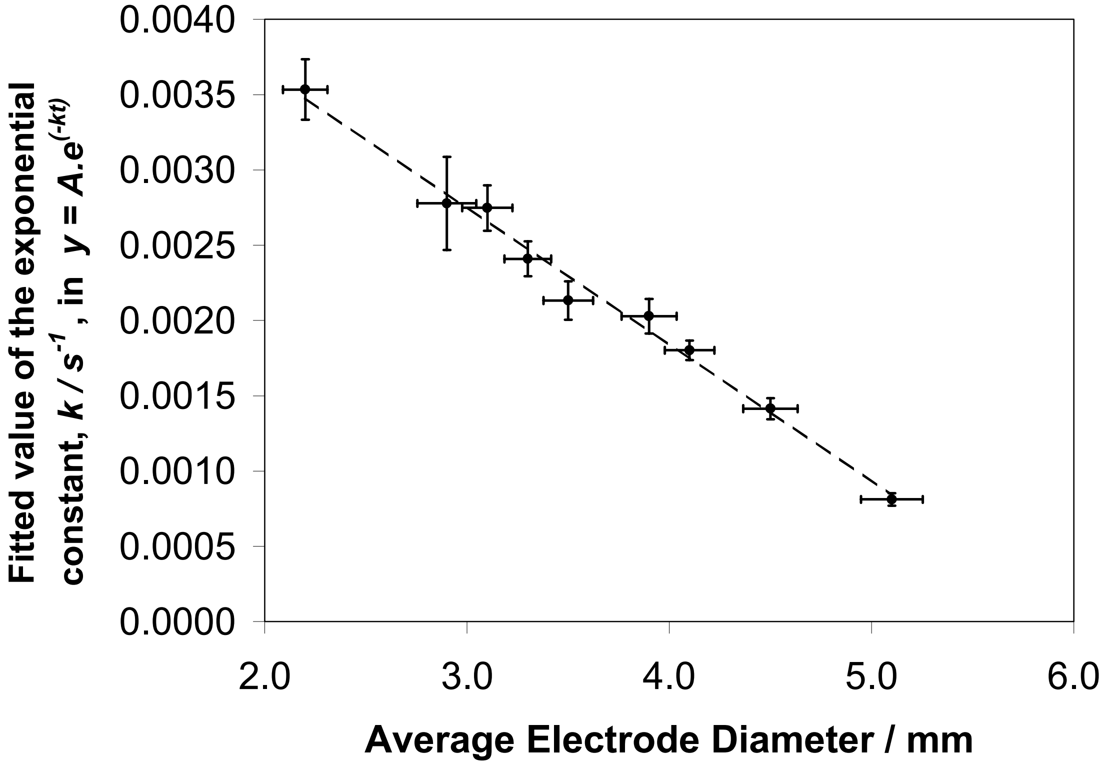

Figure 2. The value of the exponential constant, k, in the first order exponential decay function, of the type $y = Ae^{-kt}$, fitted to the potential decays of the Ag/AgCl reference electrodes in Figure 1. The uncertainty in the value of the exponential constant is produced by adding in quadrature the average uncertainty in an individual fitting to the standard deviation of the range of exponential constants obtained for each electrode diameter from repeated experiments.

Additional electrochemical impedance measurements, plotted in Figure 3, have shown that, with increasing electrode size, the resistive characteristics of the electrode increase as expected.

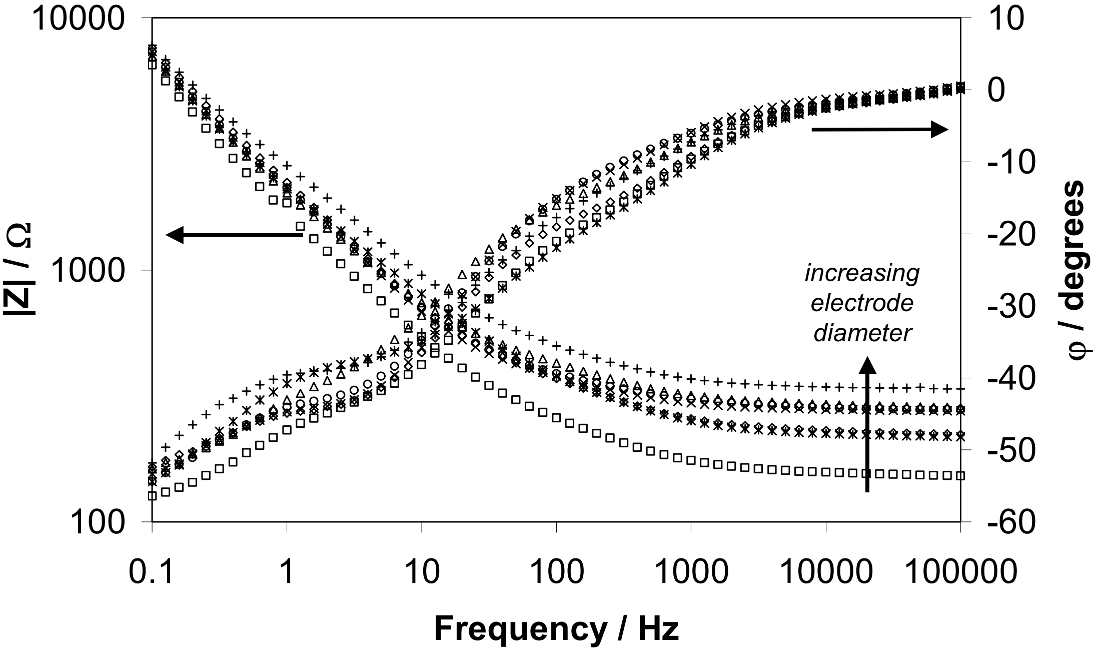

Figure 3. Plots of Impedance modulus (|Z|) and Phase Angle (φ) as a function of modulation frequency for electrochemical impedance measurements (modulation amplitude, 10mV) performed at open circuit potential in 0.01 M HCl for Ag/AgCl electrodes of diameter 2.2mm (□), 3.1mm (✳), 3.5mm (◇), 3.9mm (×), 4.1mm (○), 4.5mm (△) and 5.1mm (+).

However there is no significant change in the shape of the impedance response suggesting that there is little change in electrode pore structure with increasing size. This indicates that increasing decay time observed with increasing size of electrode is primarily due to an increase in the physical size of the electrode and not changing structural characteristics.

4. Conclusions

The transfer of porous electrodes such as Ag/AgCl between electrolytes can lead to transient shifts in the reference potential that can have a significant impact of the accuracy of, for example, Harned Cell measurements. These potential differences can be large and decay as an exponential function with the decay rate being empirically proportional to the electrode size. It is proposed that increasing decay time observed with increasing size of electrode is primarily due to an increase in the physical size of the electrode and not its changing structure or porosity. These results suggest the presence of a micro-porous structure in the electrodes that limits the rate at which traces of any previous solutions are diluted by any new solution environment.

The nature of the chemical reactions and diffusion gradients during this potential decay are extremely complex and involve reacting, dynamic, spherical phase boundaries with mixed potential phenomena and complex concentration gradients. More experimentation is required to understand fully the nature of the system. However the observation of large transient potential differences do have serious implication for the accurate operation of the Harned cell and lead to the formulation of best practice solutions for Ag/AgCl electrode handling in primary pH measurements:

- Ideally, Ag/AgCl reference electrodes should be pre-conditioned by being allowed to equilibrate externally to the Harned Cell before use, in a solution as similar as possible to that which the electrode is about to be used in. This also avoids contamination of the solution to be measured. In this way equilibration times following transfer to the Harned Cell may be cut to less than 5 minutes.
- Harned Cell measurements should only be made once the Ag/AgCl electrode have fully equilibrated in the Harned Cell.
- For either pre-conditioning, or equilibration within the Harned Cell, it is suggested that a minimum of three hours be allowed for Ag/AgCl reference electrodes to equilibrate properly. Very large electrodes may need more time. If possible, it is best to allow the electrodes to equilibrate over night.
- Ag/AgCl electrodes should be manufactured to be as small as possible, to minimise the equilibration time required, consistent with still exhibiting stable reference potentials.

Failure to implement these recommendations may compromise the accuracy of primary pH measurements. The adverse effect of these procedures would be to decrease the throughput of primary buffer certification, but this must be tolerated in order to maintain measurement quality at the primary level. The use of different designs for Ag/AgCl electrodes, such as extended cylindrical geometries, rather than a spherical geometry, should help to minimise possible stabilisation problems.

5. Acknowledgement

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