An Improved Approach for Fabricating Ag/AgCl Reference Electrodes

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pH measurement

• Concept of pH was first introduced by Sørensen in 1909
• One of the most commonly used analytical determinations
  - Chemical and drug manufacture
  - Blood gas determinations
  - Effluent discharge control
  - Food and drink processing
  - Water purity
• Essential to ensure the validity and traceability
Traceability

- Relating a measurement result to a reference through an unbroken chain of comparisons, all having stated uncertainties
- Standards prepared at NMIs traceable to the SI and measured using a primary method
International comparisons

8 key comparisons in the last decade
(K9, K9.2 K17, K18, K18.1, K19, K19.1, K20)
Harned cell – primary method

- electrochemical cell arrangement which does not contain a liquid junction
- relies on well characterised Ag/AgCl reference electrodes for operation
- 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

\[ \text{Pt} | \text{H}_2 | \text{buffer, Cl}^- | \text{AgCl} | \text{Ag} \]
Influence of Ag/AgCl electrode potential

- Ag/AgCl is the 2nd largest uncertainty contributor
- Repeatability: potential must be < 100 µV from the mean
- Stability: potential < 30 µV/ h
Electrode fabrication

thermal electrolytic

electrolytic
Electrode microstructure

higher purity
higher geometric surface area
higher exchange current at eqm
good stability

3 structures proposed by Janz
Stability dependent on porosity

more impurities
lower geometric surface area
lower exchange current at eqm
poorer stability
Thermal electrolytic electrodes

- Thermal electrolytic electrodes offer several advantages:
  - Fabrication less time consuming
  - Reduced equilibrium times
  - Low contamination risk
  - Portability

- Annealing redistributes and destroys crystallographic defects, producing an homogenous material

- Annealing should remove strains and improve structural uniformity, improving performance

Requirement: improve long term stability and repeatability
AgCl distribution

[Images showing the distribution of AgCl with scale bars of 1 mm]
Anodisation – constant current density
Anodisation – constant current
Transient anodisation signatures
Transient anodisation signatures
Ag/AgCl potential measurements

![Graph showing potential over time](Image)
Impedance spectroscopy
SEM – constant current / potential
Conclusions

- New self-limiting approach for fabricating Ag/AgCl electrodes
- Superior repeatability
- Improved conductivity due to microstructure
- Transient current data provides information in microstructure
- Far-reaching implications for pH measurement
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