An Improved Approach for Fabricating Ag/AgCl Reference Electrodes

28th CITAC members' meeting

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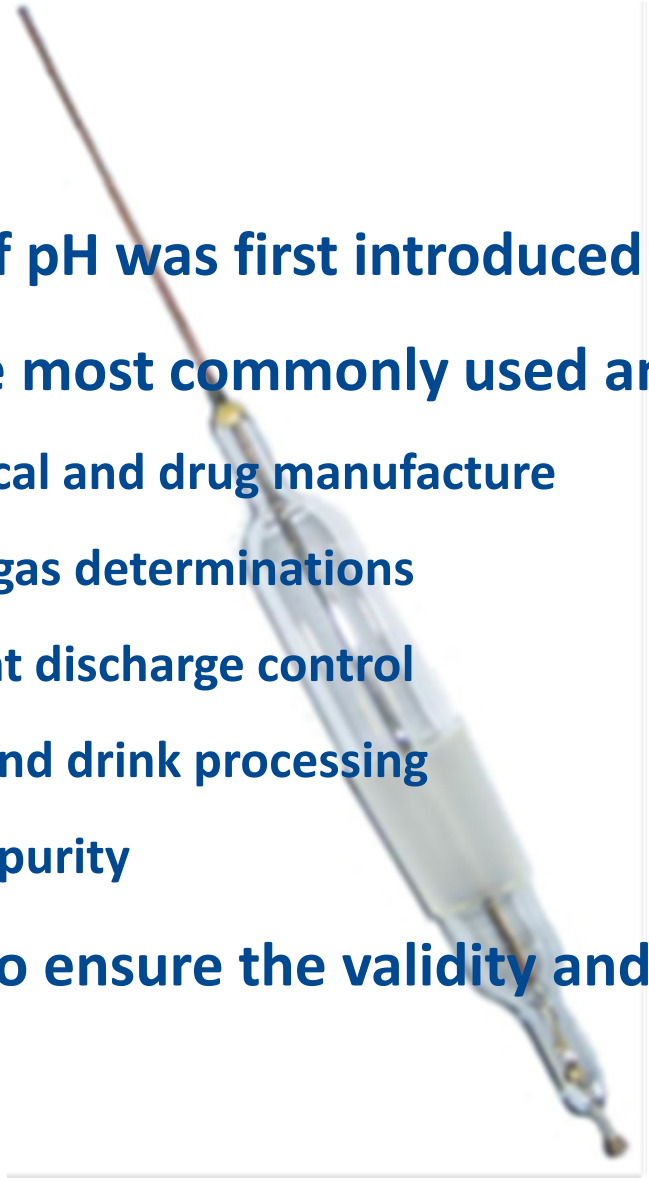
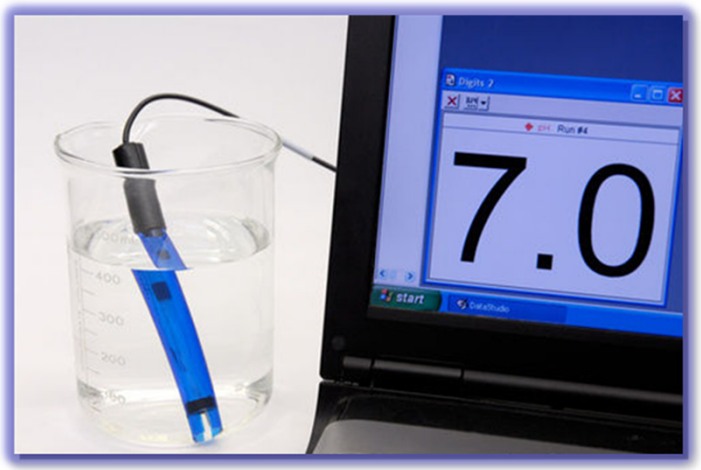
Hotel Mercure Paris Porte de St Cloud, Paris

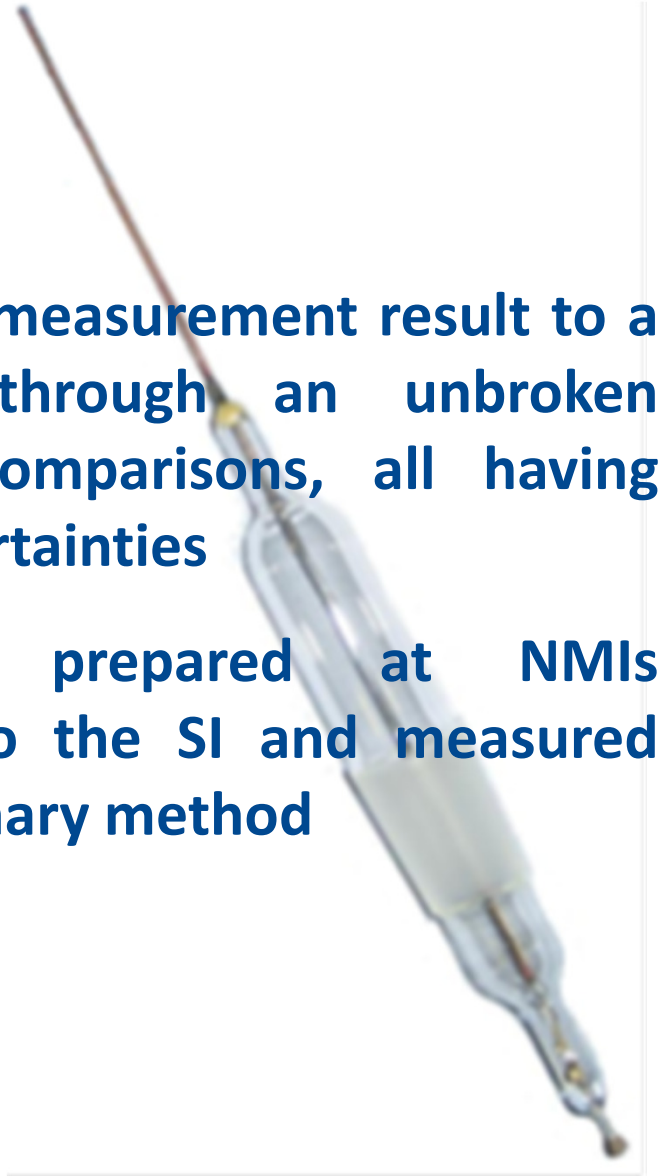
pH measurement



- 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

IUPAC
Definition of pH and Harned cell

↓

NMIs
Primary buffers

↓

Buffer manufacturers
Secondary buffers

↓

Calibration labs
Glass electrode buffers

↓

Routine pH measurements
Commercial glass pH electrodes

International comparisons

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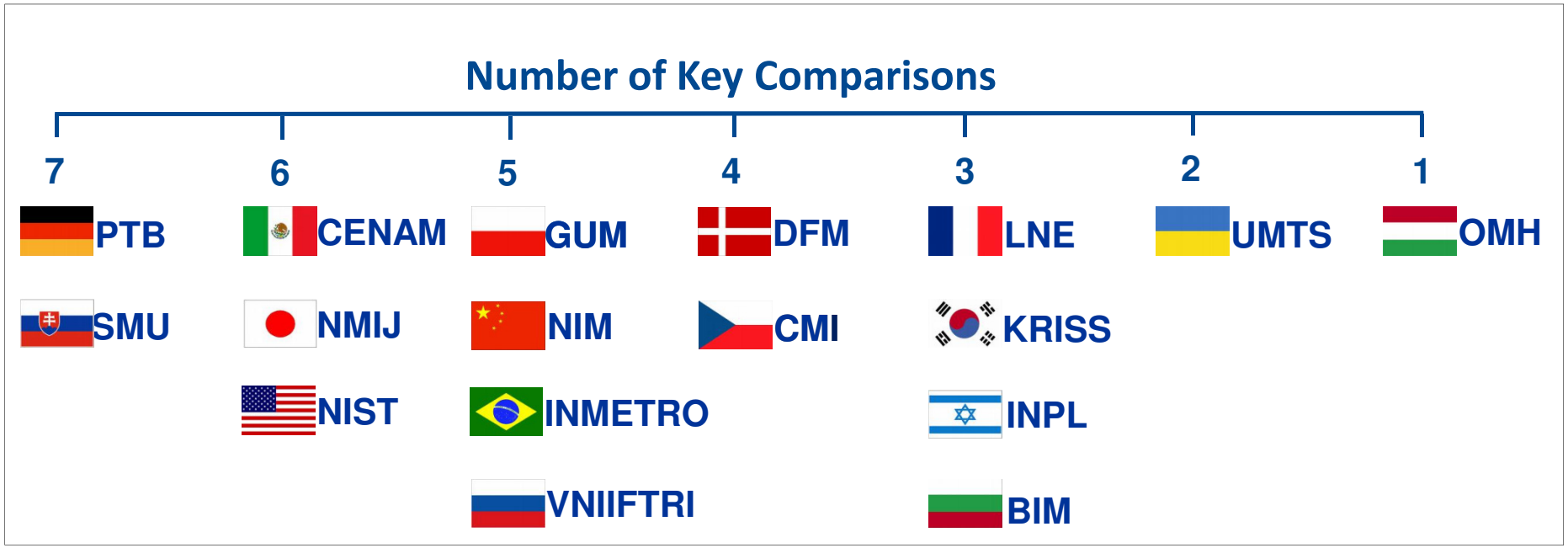
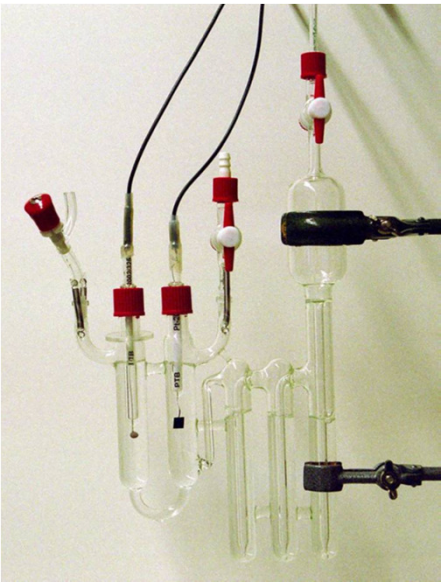
8 key comparisons in the last decade

(K9, K9.2 K17, K18, K18.1, K19, K19.1, K20)



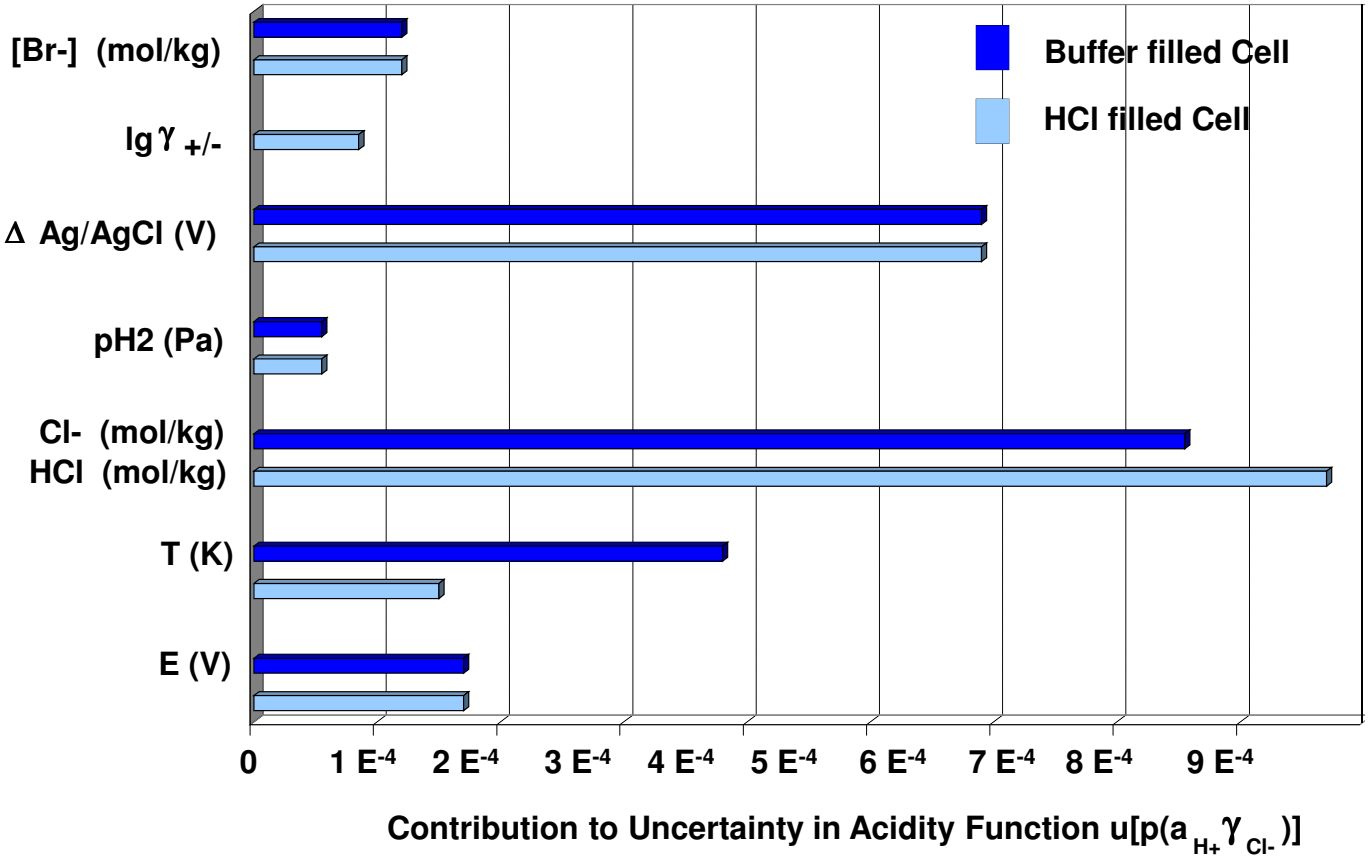
Harned cell – primary method



$Pt|H_2|buffer, Cl^-|AgCl|Ag$

- 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

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

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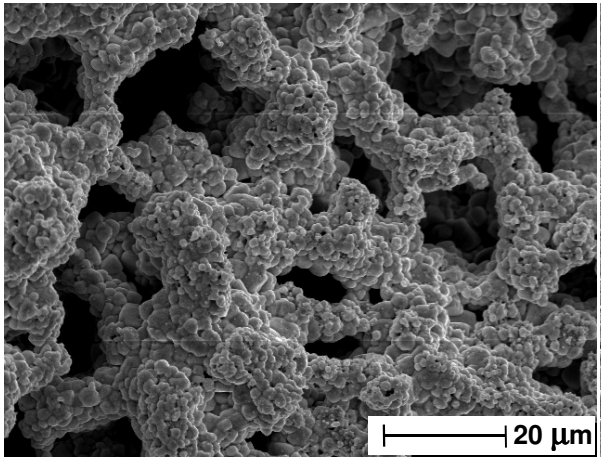
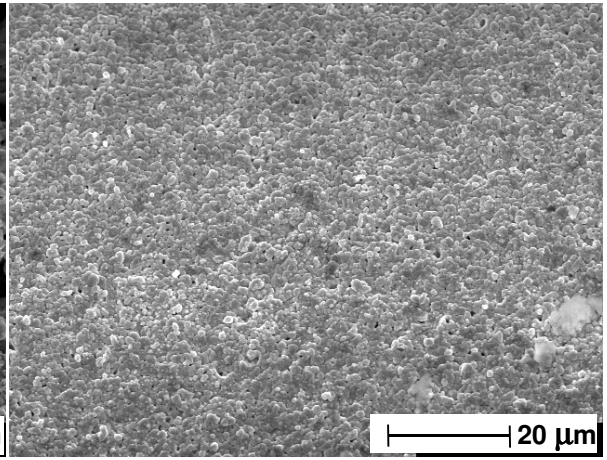
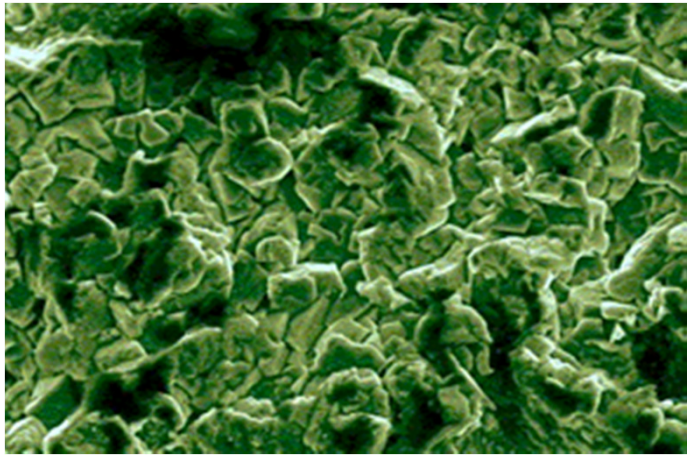
thermal electrolytic

electrolytic

Electrode microstructure







higher purity

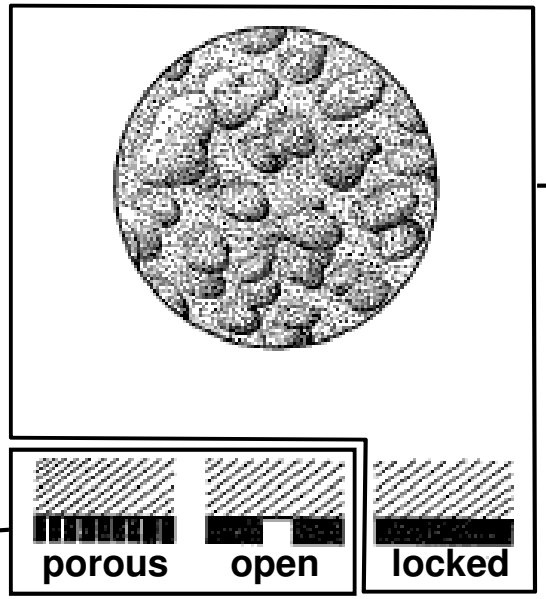
higher geometric surface area

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

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- Thermal electrolytic electrodes offer several advantages:

  - Fabrication less time consuming

  - Reduced equilibrium times

  - Low contamination risk

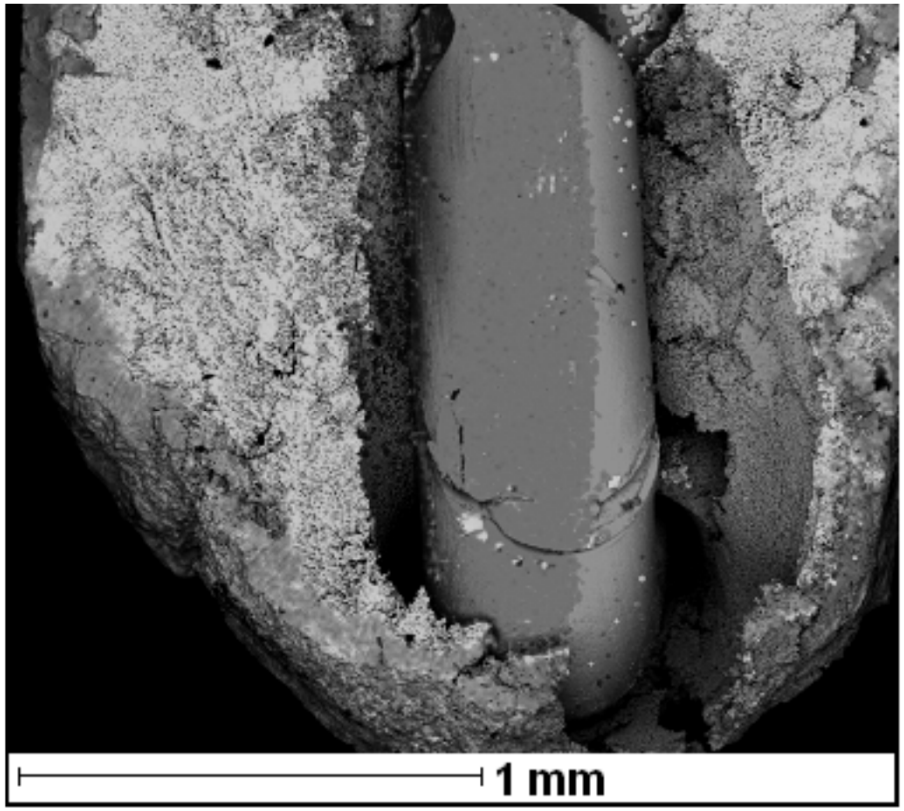
  - Portability

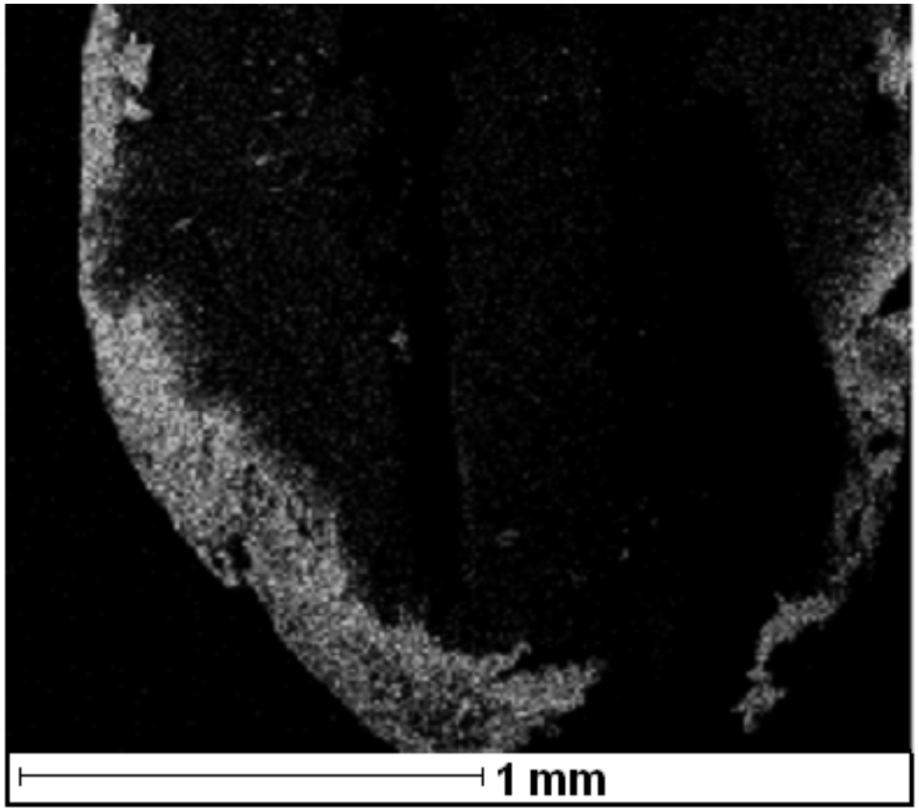
- Annealing redistributes and destroys crystallographic defects, producing an homogenous material

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

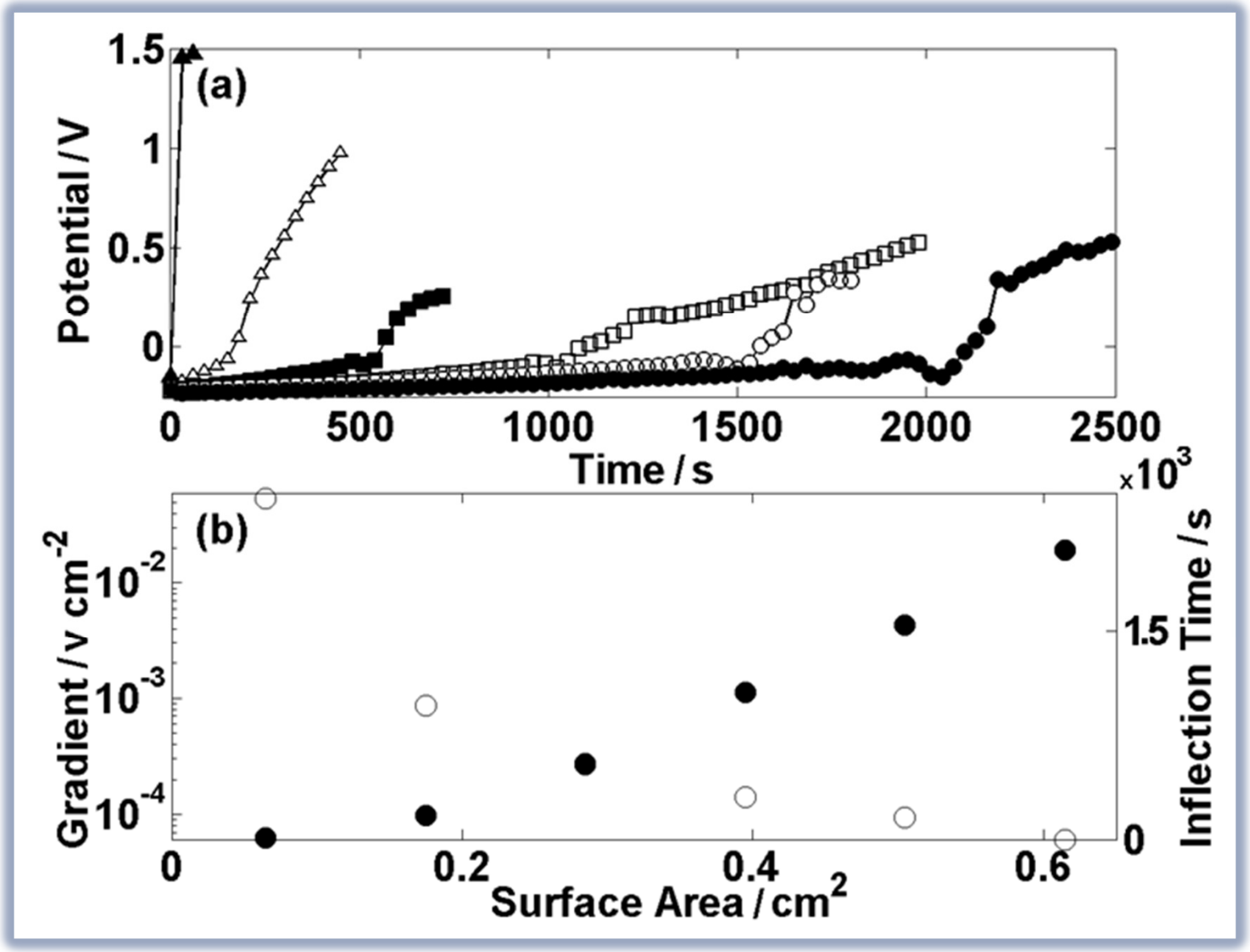
Requirement: improve long term stability and repeatability

AgCl distribution

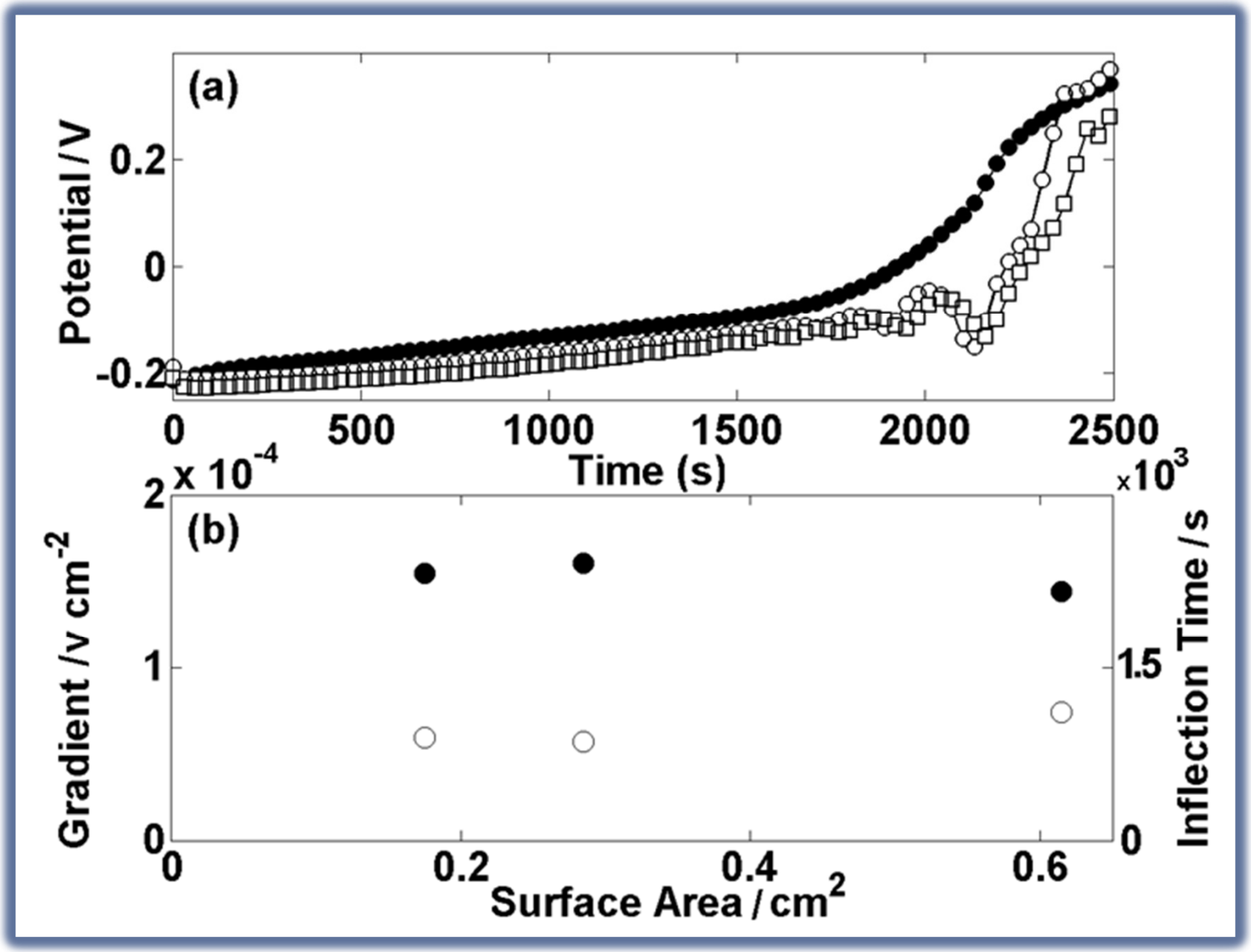




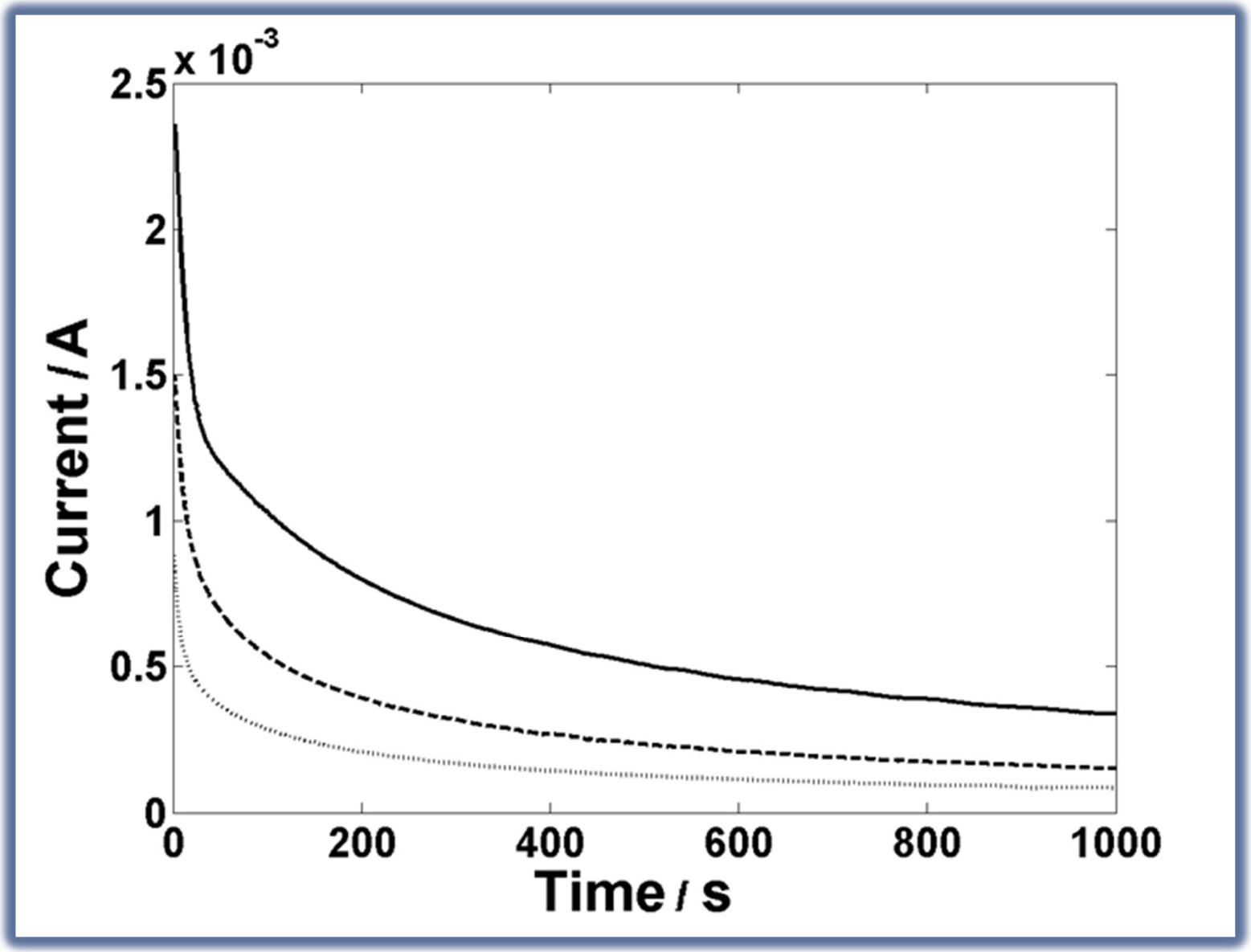
Anodisation – constant current density



Anodisation – constant current



Transient anodisation signatures



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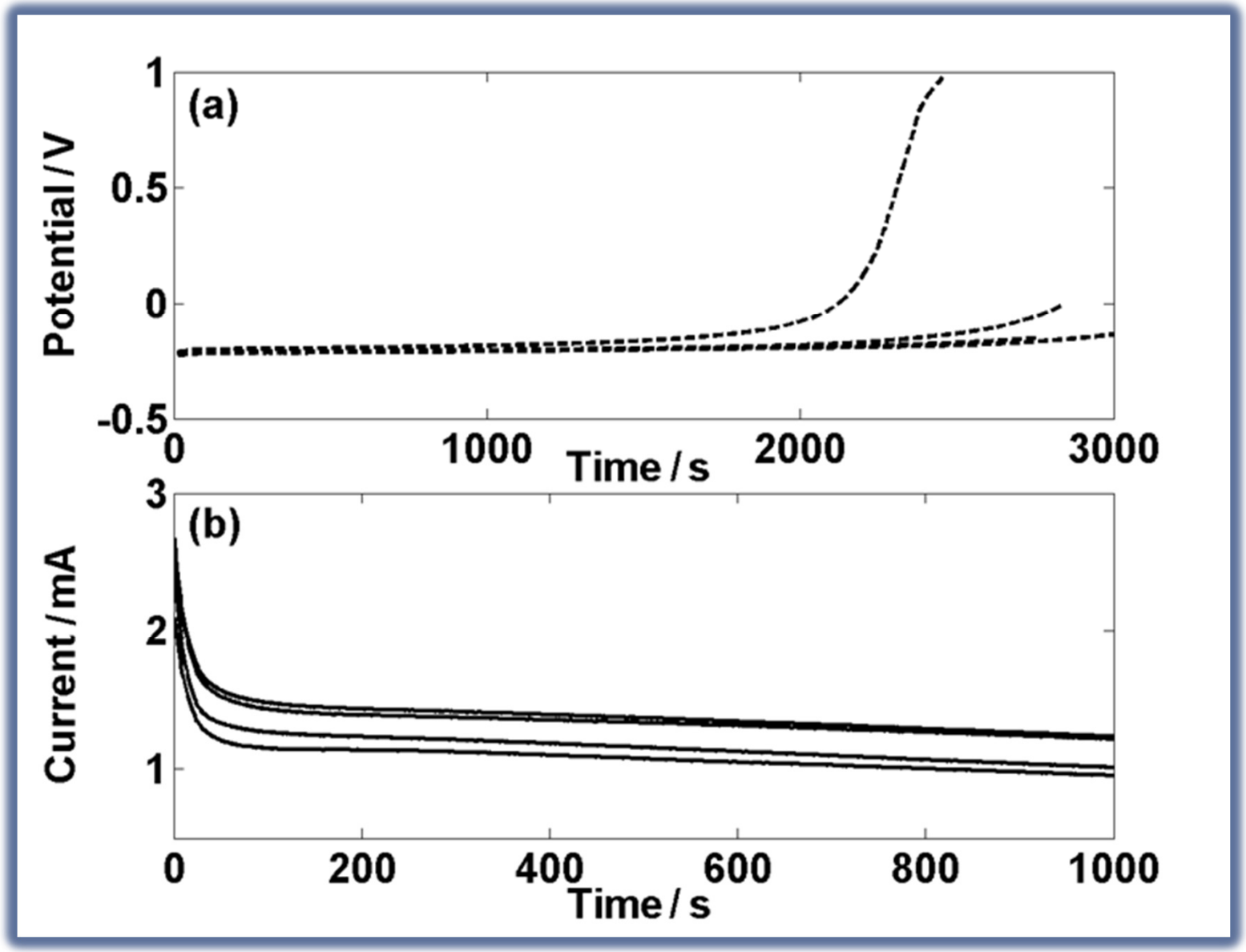
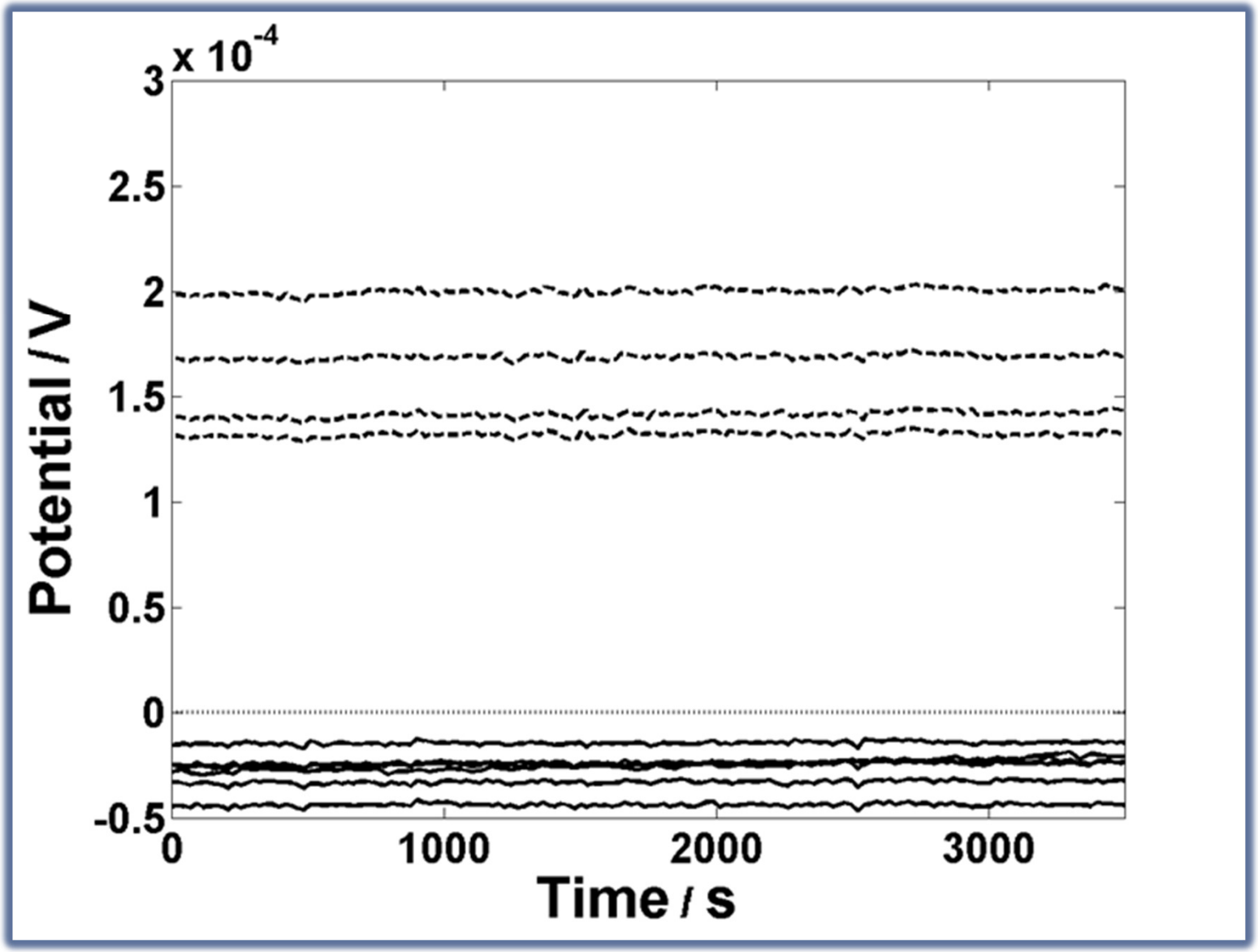
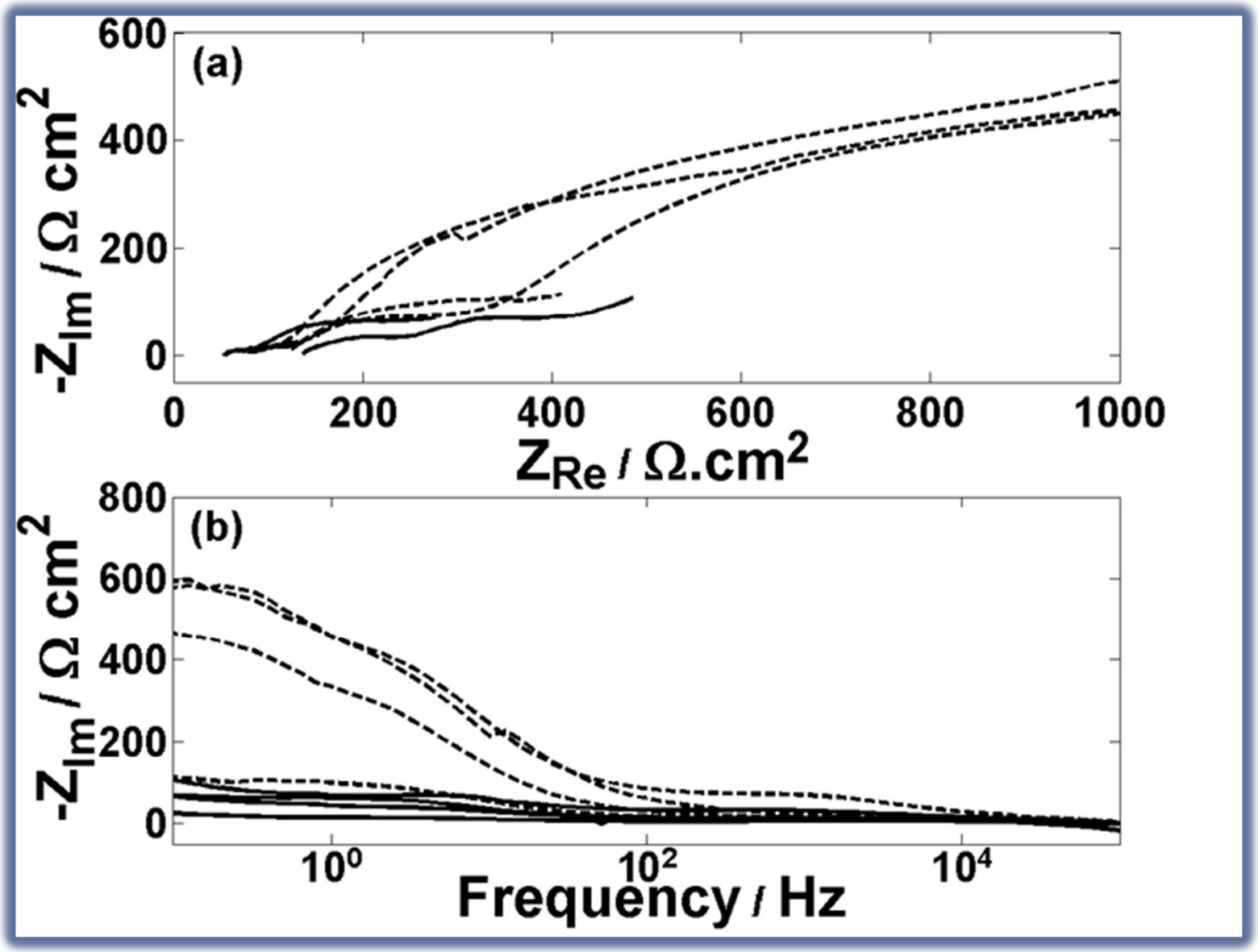


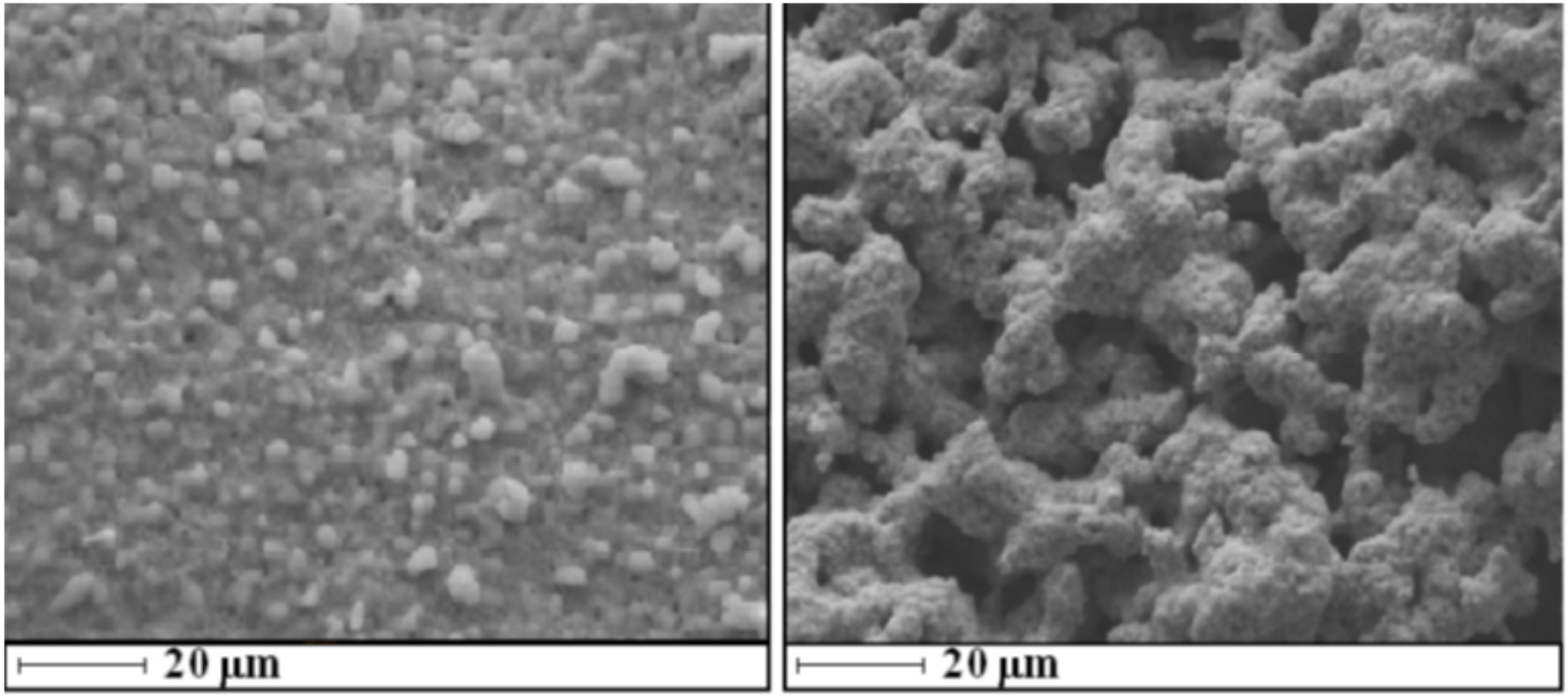
Ag/AgCl potential measurements



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

Acknowledgements

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