AlGaN/GaN based pH-sensitive Field-Effect Transistors for nonaqueous solutions

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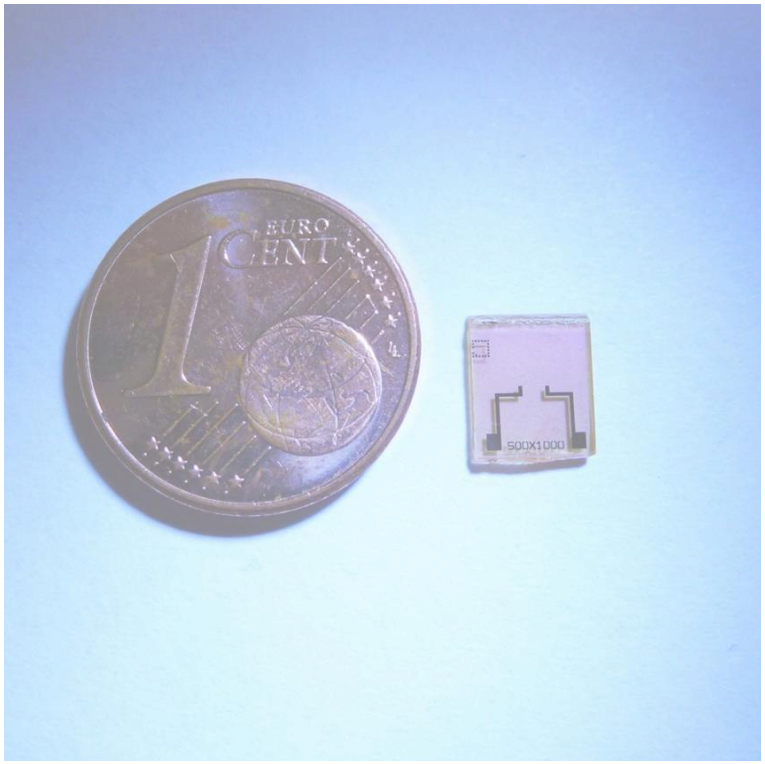

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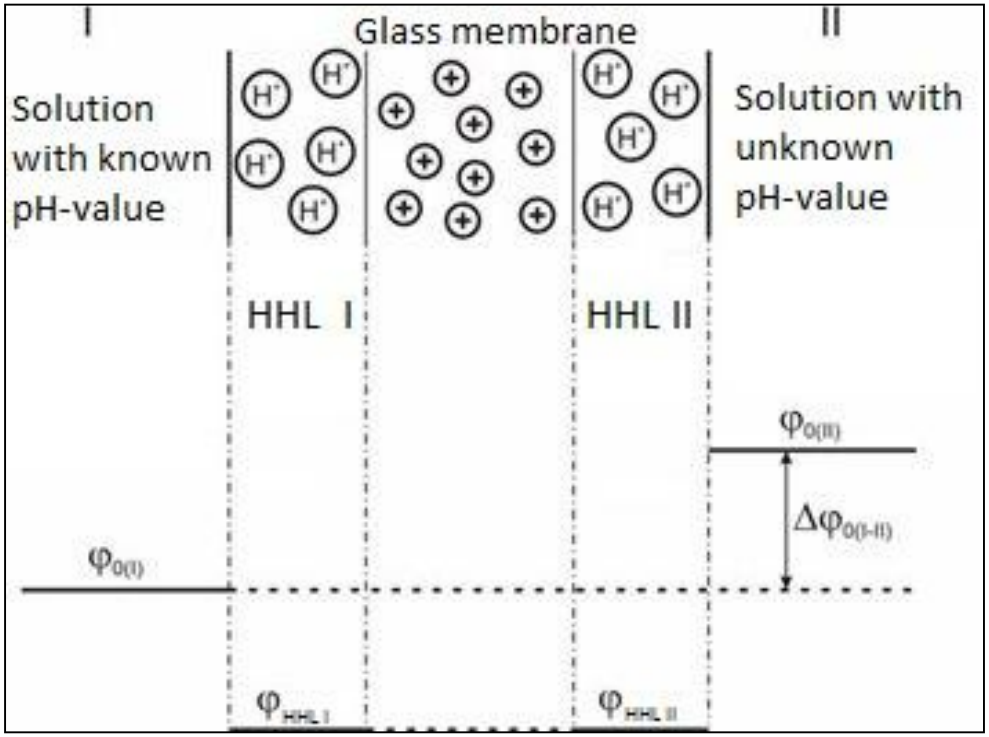
Motivation

- Non-aqueous solvents ≠ water
  - Permittivity, Conductivity, Viscosity, Autoprotolysis constants, acidity, basicity …
- Concept of Brønsted acid-base-theory can still be applied
  - pH = -log a(H^+)
- Applications:
  - Acidity in fuel → quality criterion
  - Chemical reactions
- Measurements can be done with glass electrode but…

Motivation

- glass electrode disadvantages
  - Bulb dehydration
  - Bulb contamination
- Lead to
  - unstable readings
  - Long response times



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Motivation

- glass electrode disadvantages
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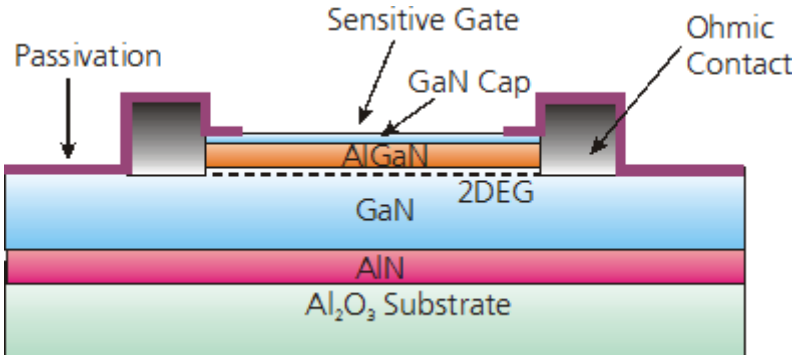
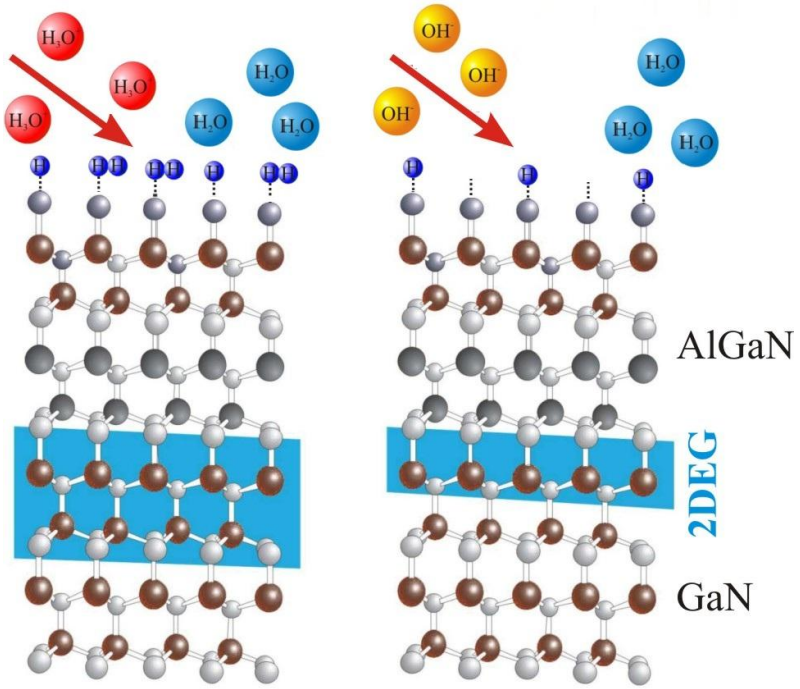
- ISFET fast response
- Smooth surface can be cleaned well
- ISFET can be incorporated in ceramic structure → stability
- GaN surface chemically stable *

* St. Linkohr, W. Pletschen, St.U. Schwarz, J. Anzt, V. Cimalla, and O. Ambacher: „CIP (cleaning-in-place) stability of AlGaN/GaN pH sensors", J. Biotechnol. 163 (2013) 254-361.

Sensor principle

- 2D electron gas at GaN/AlGaN interface
- Native oxide at surface
  - → Hydroxyl groups → Proton selectivity





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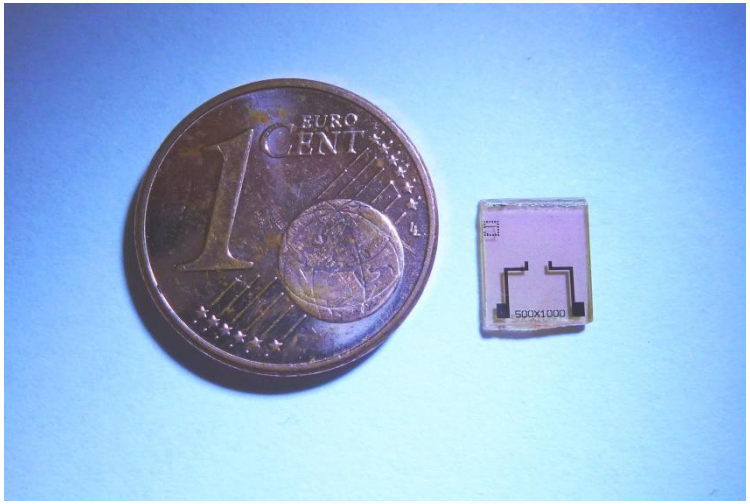
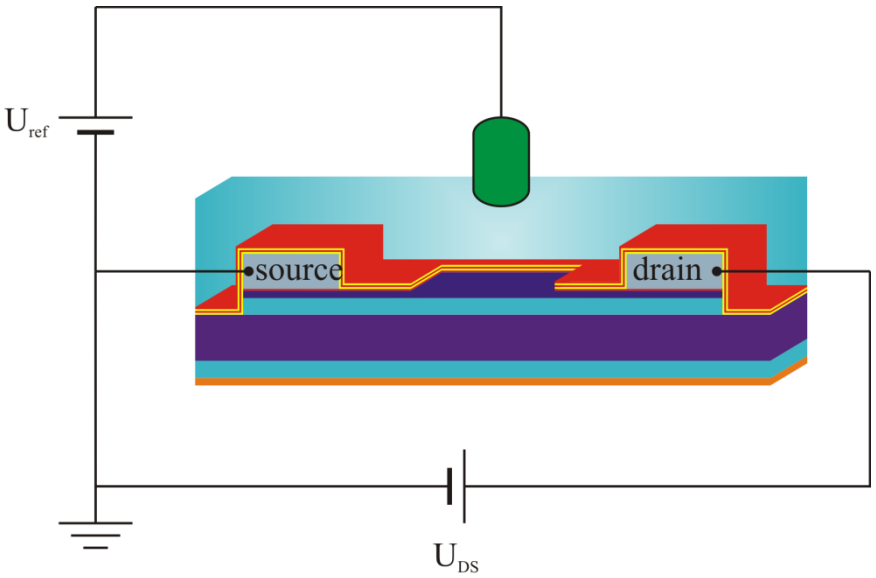
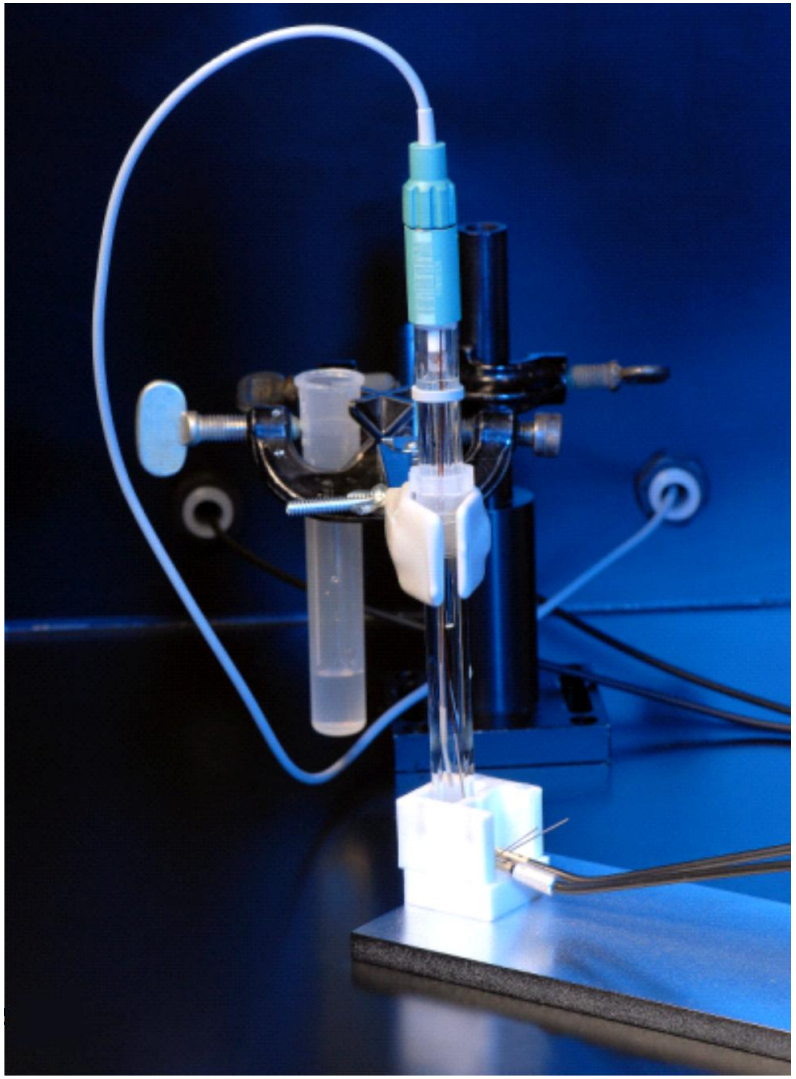
Experimental setup







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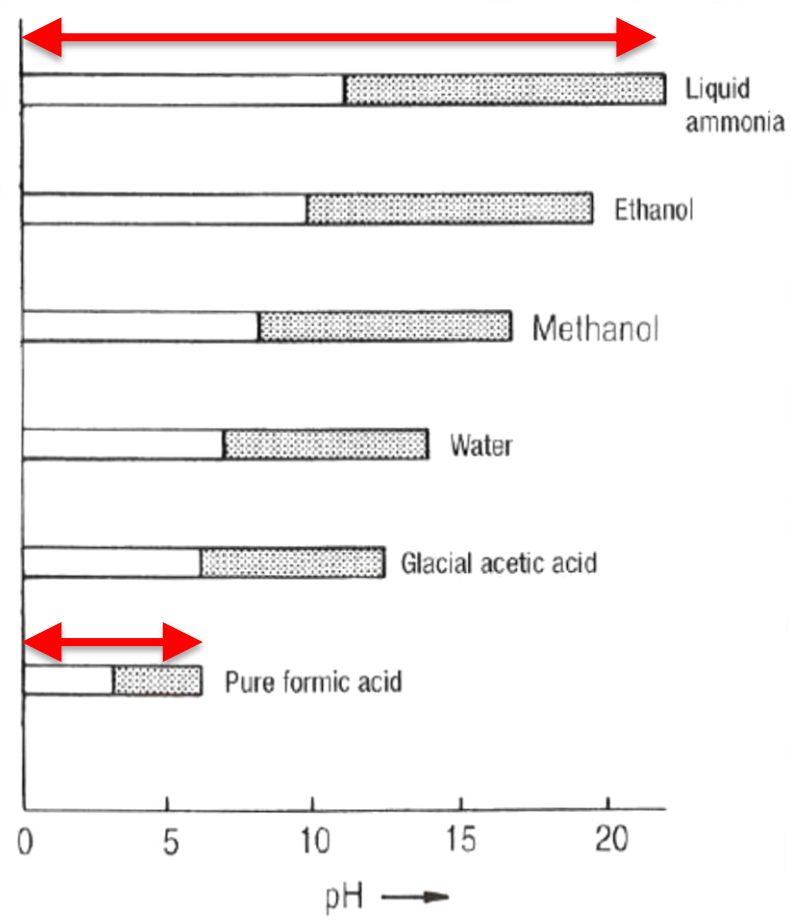
pH-scales in different solvents

- pH = -log a(H^+)
  - **Width pH-scales** ≈ pK_{solv}
    - E.g. pK_{H2O} =14, $pK_{Ammonia}$ = 22



Hamann, Hamnett, Vielstich – Electrochemistry (2007)

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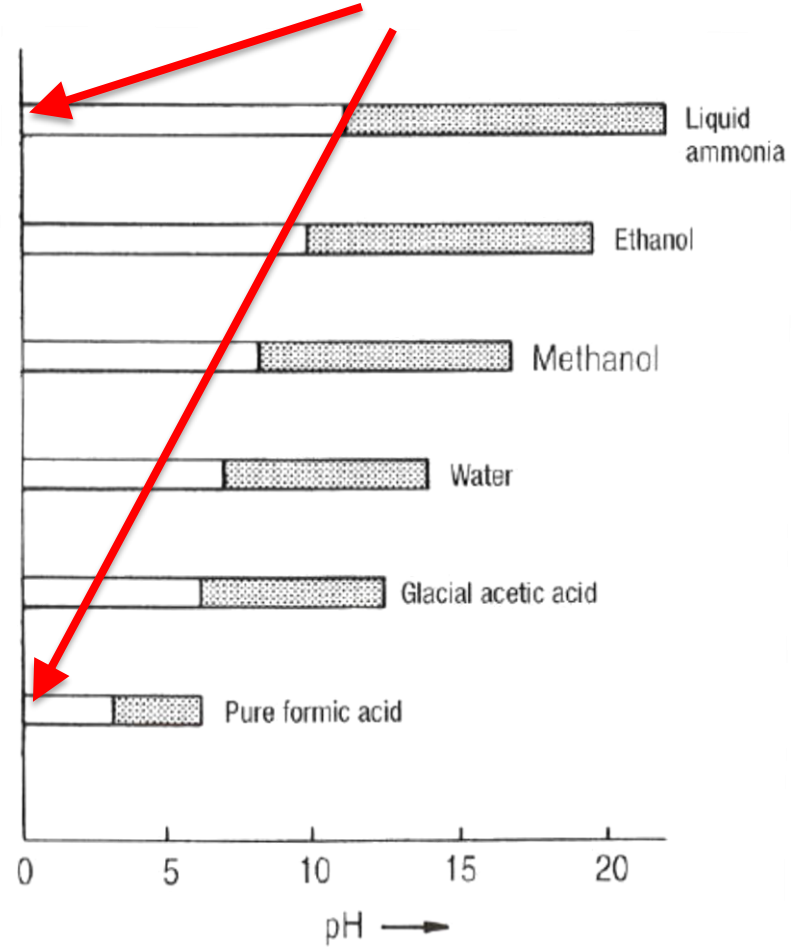
  - Activity does not mean **reactivity**!



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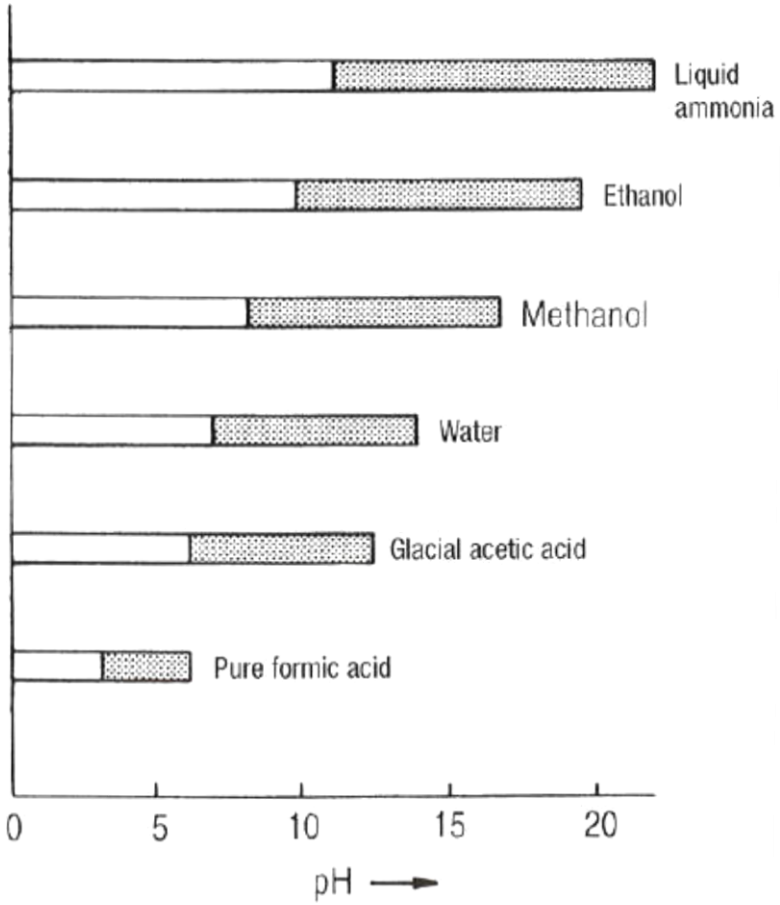
  - Activity does not mean reactivity!
  - **Different for every solvent composition**



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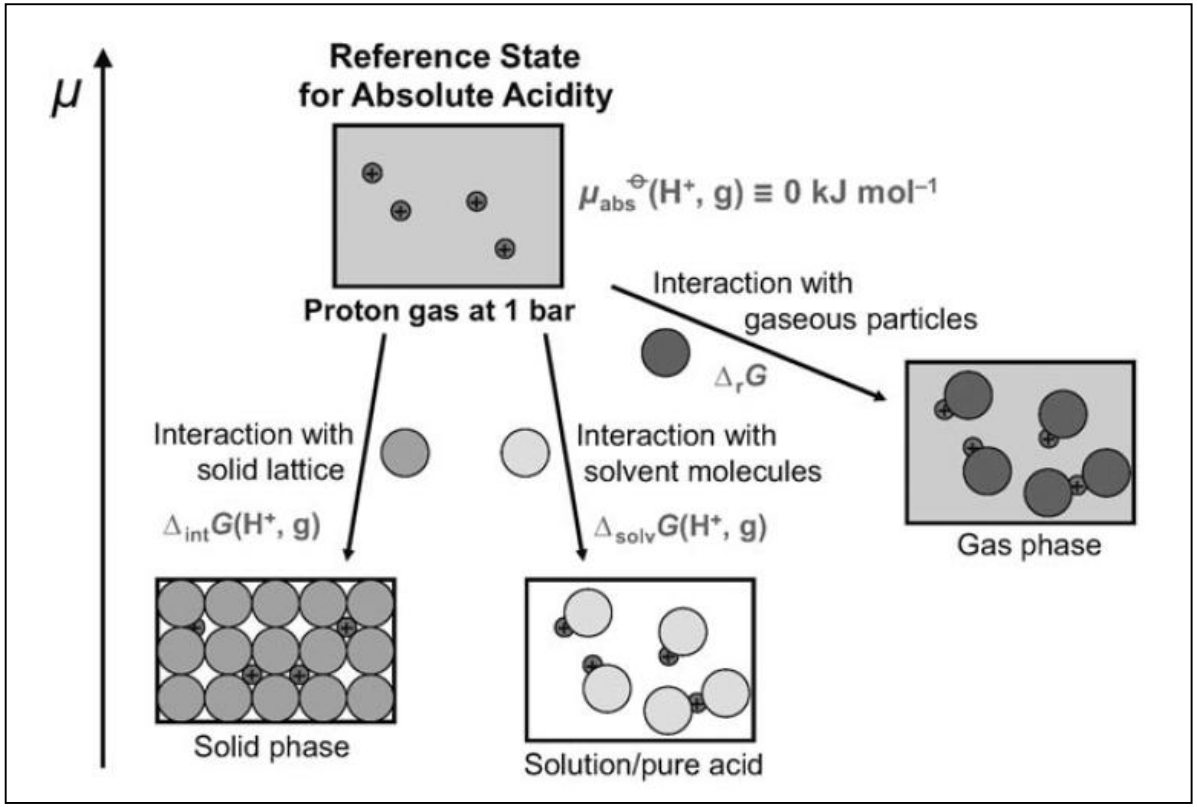
Unified pH-scale



* For $\Delta pH = -\Delta \lg a(H^+) = 1$ holds: $\Delta\mu_{abs}(H^+, solv) = RT\Delta \ln a(H^+) = 2.303\,RT \lg 0.1 = -5.71$ kJ mol^{-1} at $T = 298.15$ K.

Himmel, D., Goll, Sascha K., Leito, I. and Krossing, I. (2010),
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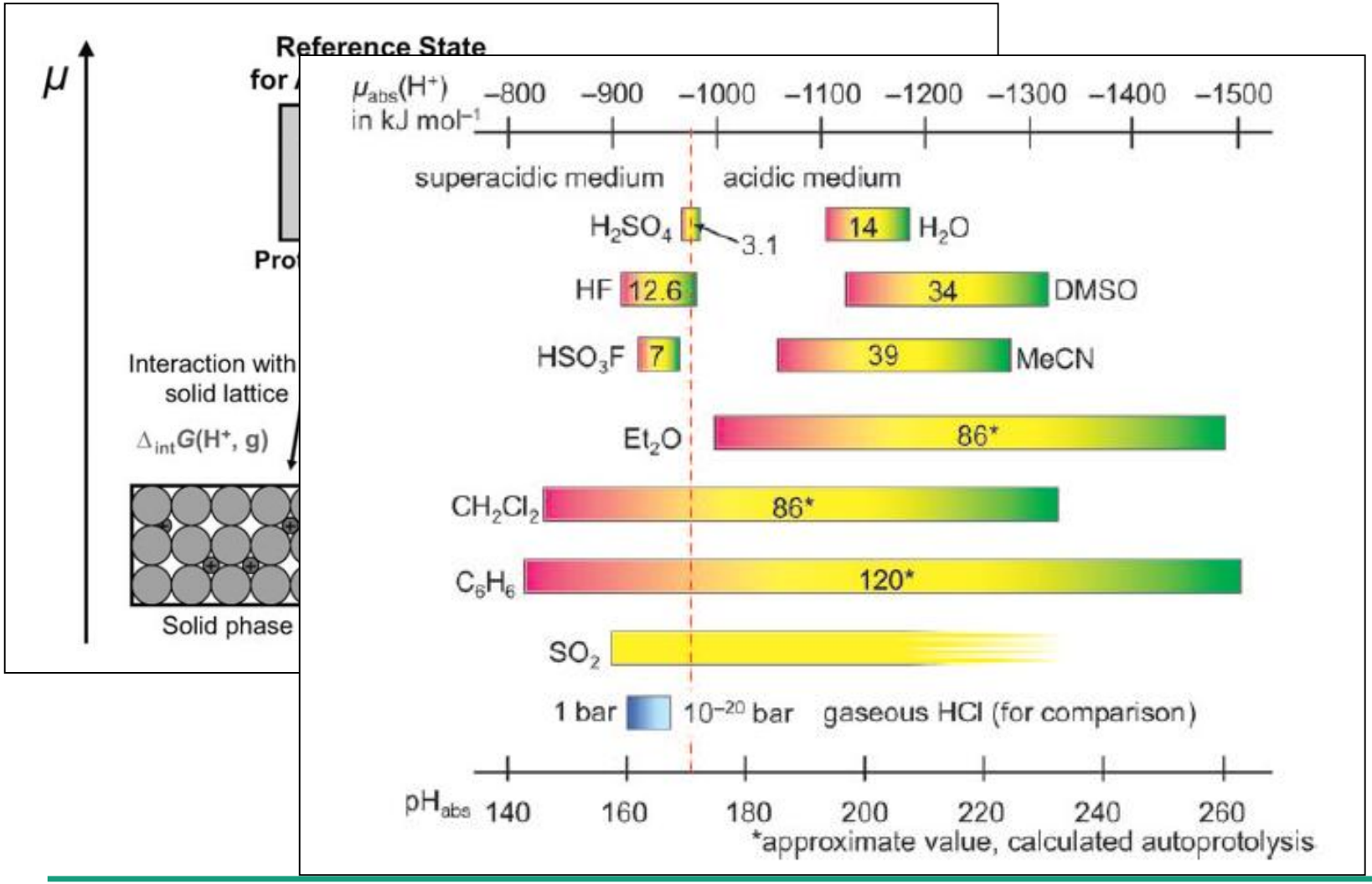

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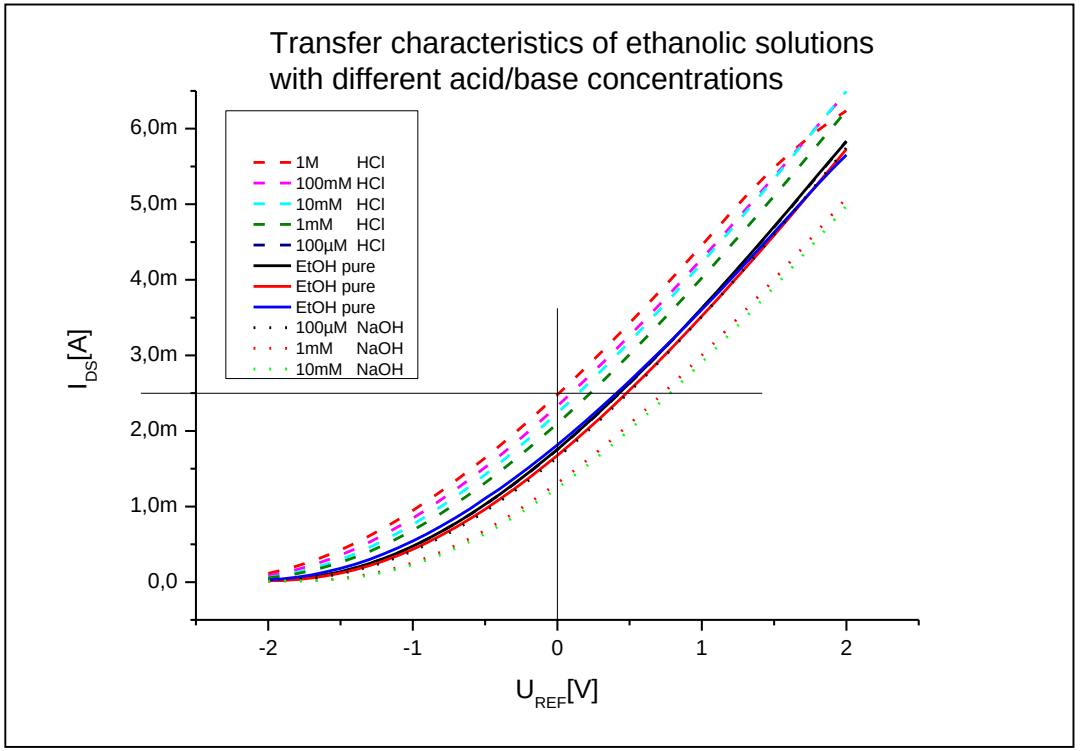
Acidity measurements in ethanolic solutions



- Evaluate sensitivity S_U @ I_{DS} = 250 mA

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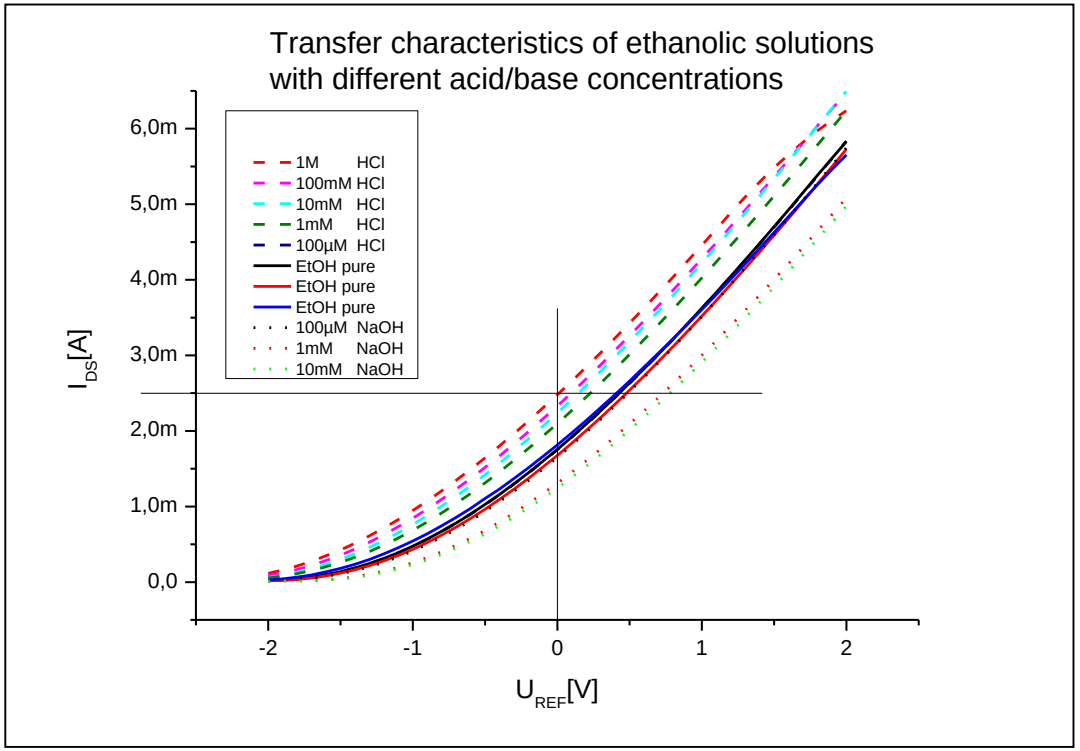

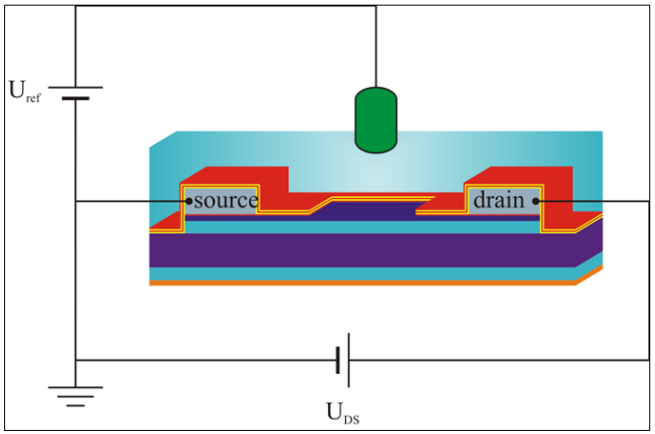

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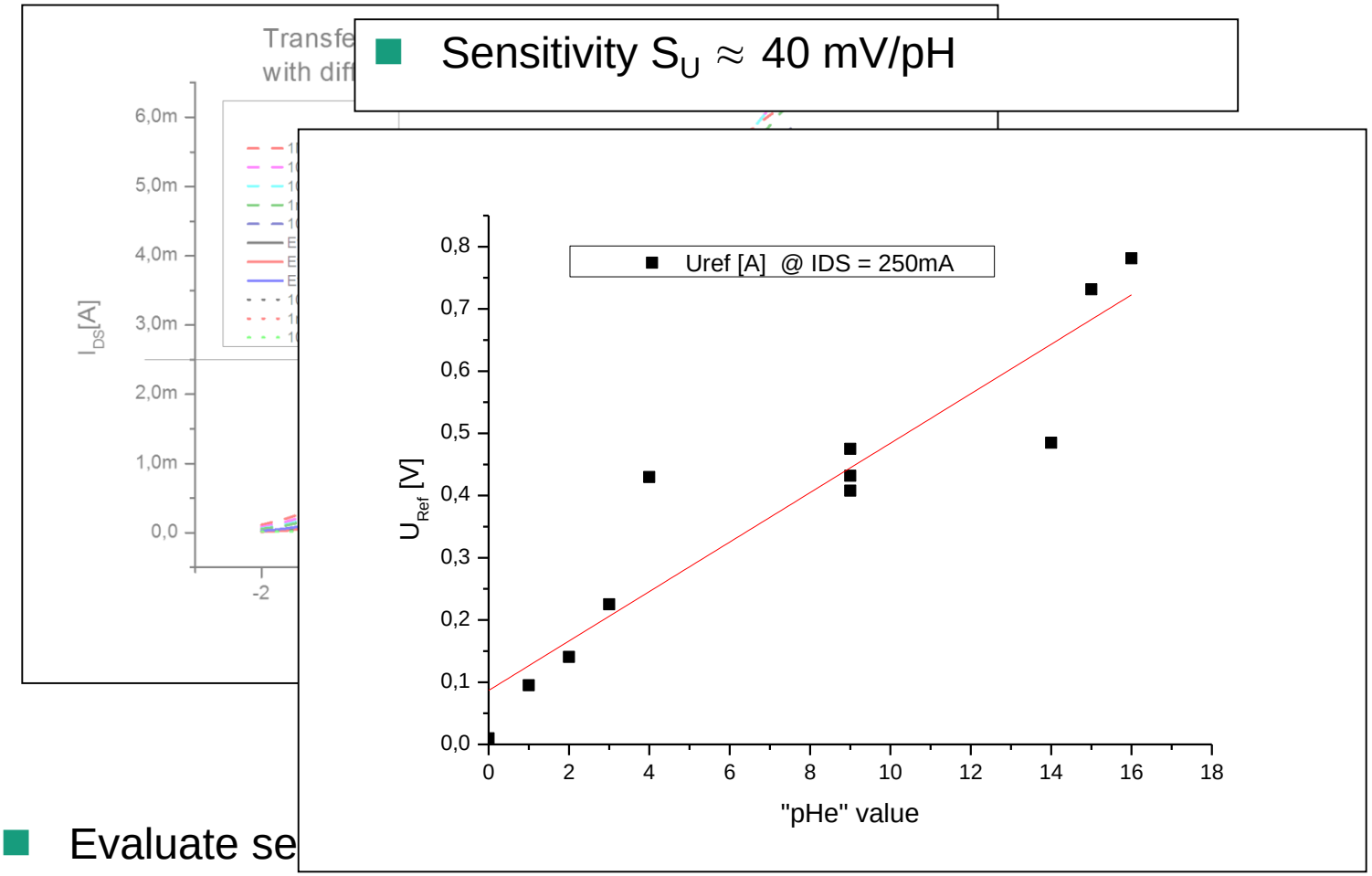
Acidity measurements in ethanolic solutions

- Sensitivity $S_U \approx 40$ mV/pH



- Evaluate se

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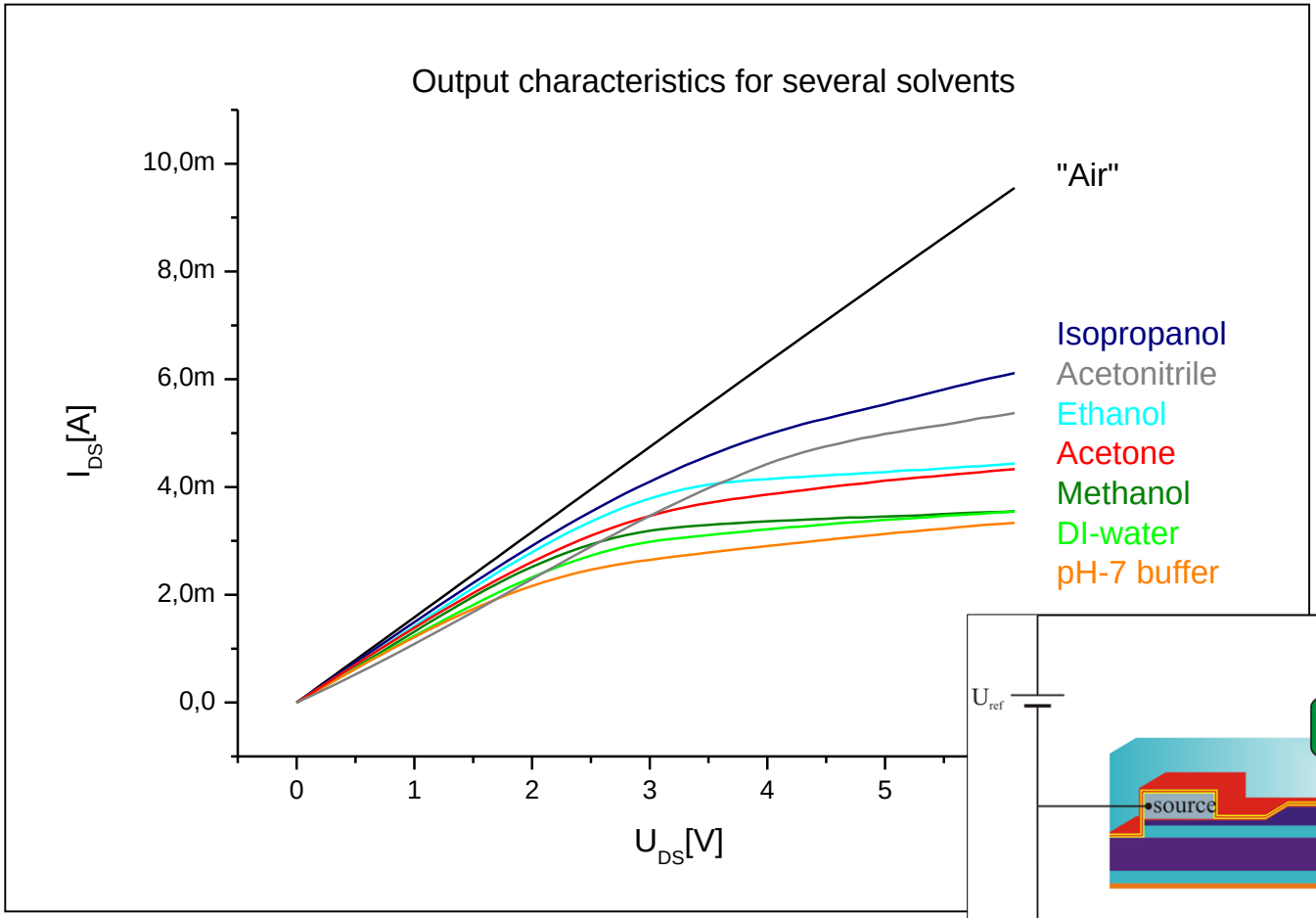
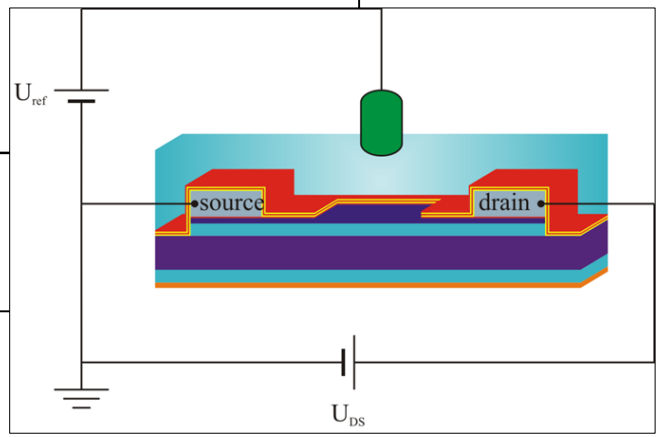
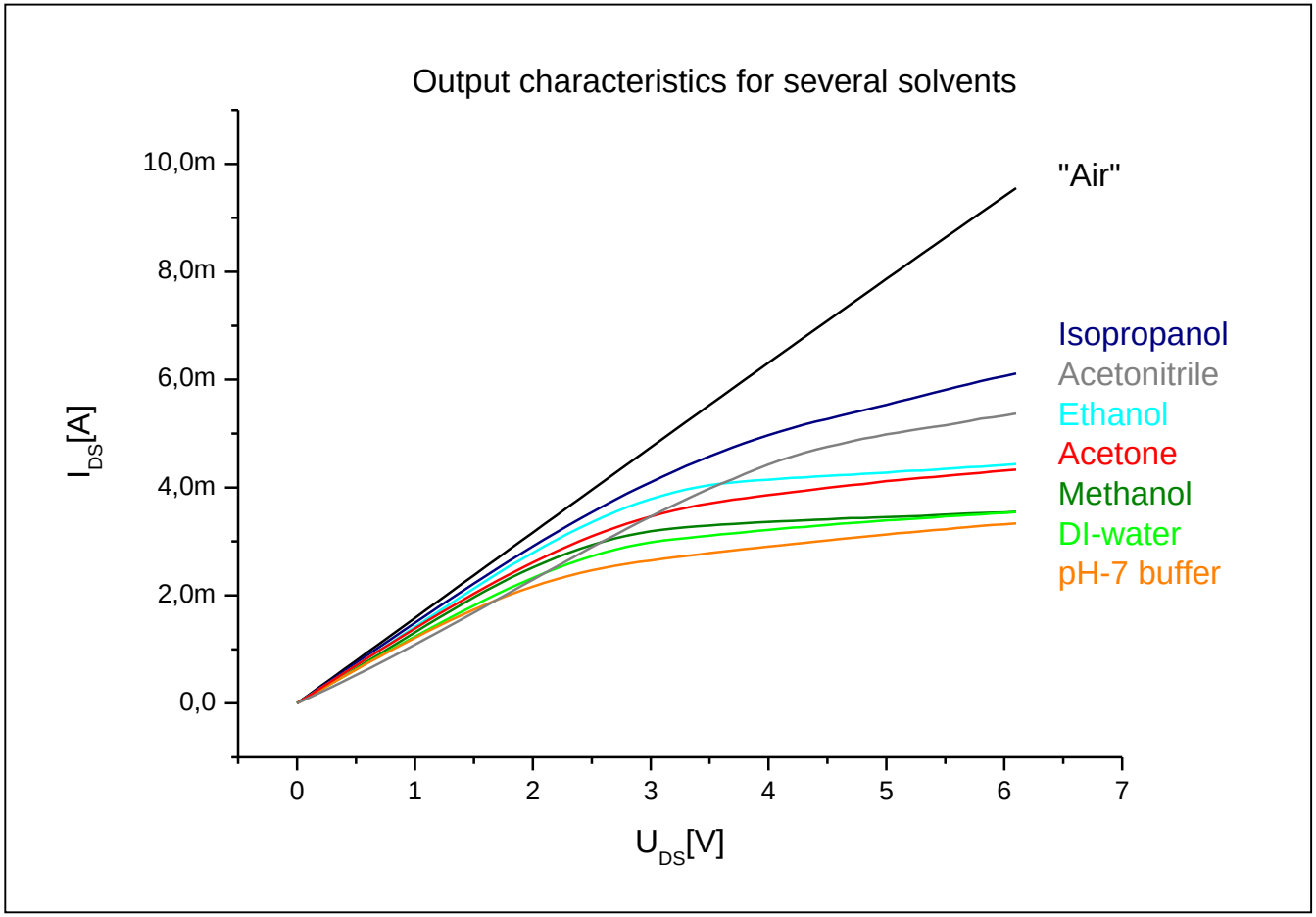
Measuring different solvents





Measurement without reference electrode

Measuring different solvents



Measurement without reference electrode

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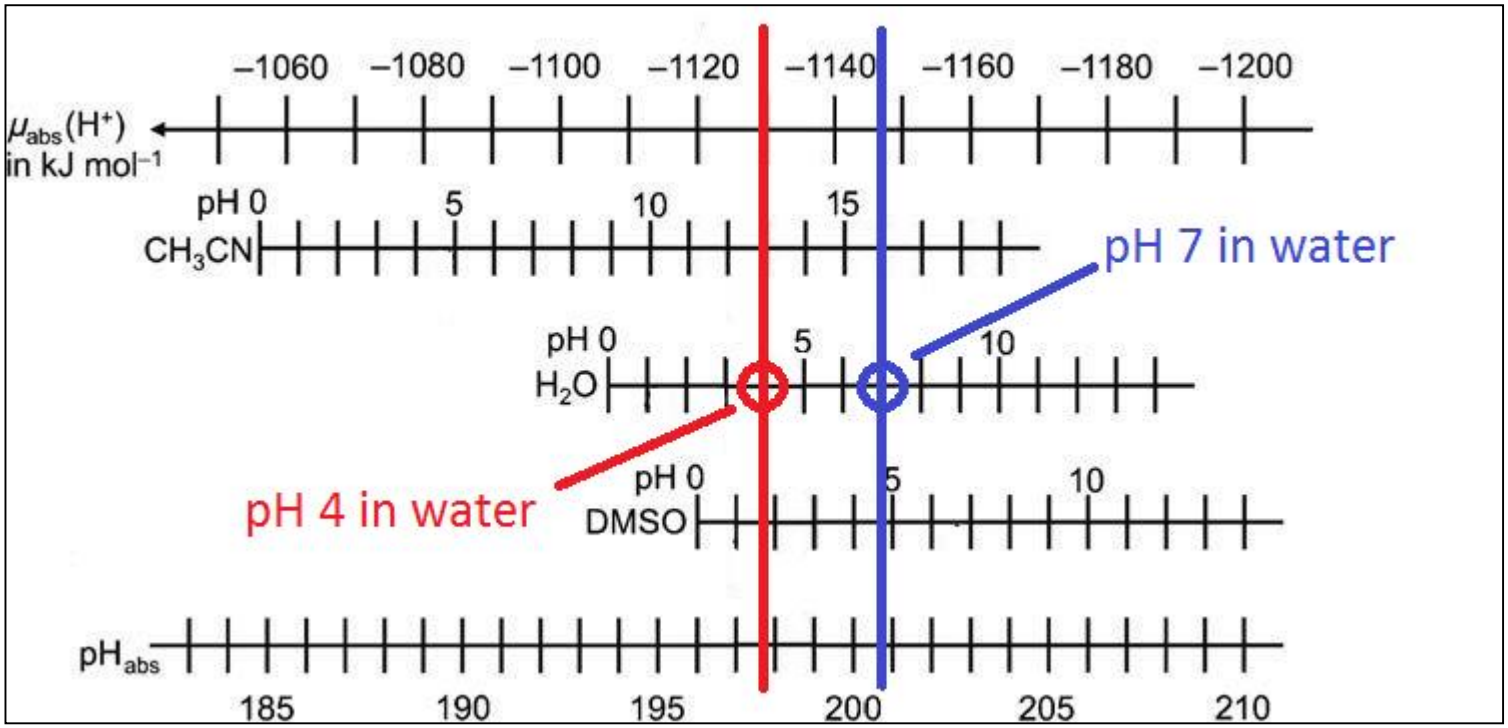
Comparing the pH-scales



- pH Values adjusted by
  - para-toluenesulfonic acid in DMSO
  - acetic acid in MeCN
- Comparison
  - Commercially available pH-buffer (aqueous)

- pH 0 in water at μ = -1105 kJ mol^{-1}
- 1 pH unit ≙ -5,71 kJ mol^{-1} *
- $\mu_{abs}(H^+,solv)=\Delta_{solv}G^{\ominus}(H^+)-[pHx(5,71kJ/mol)]$

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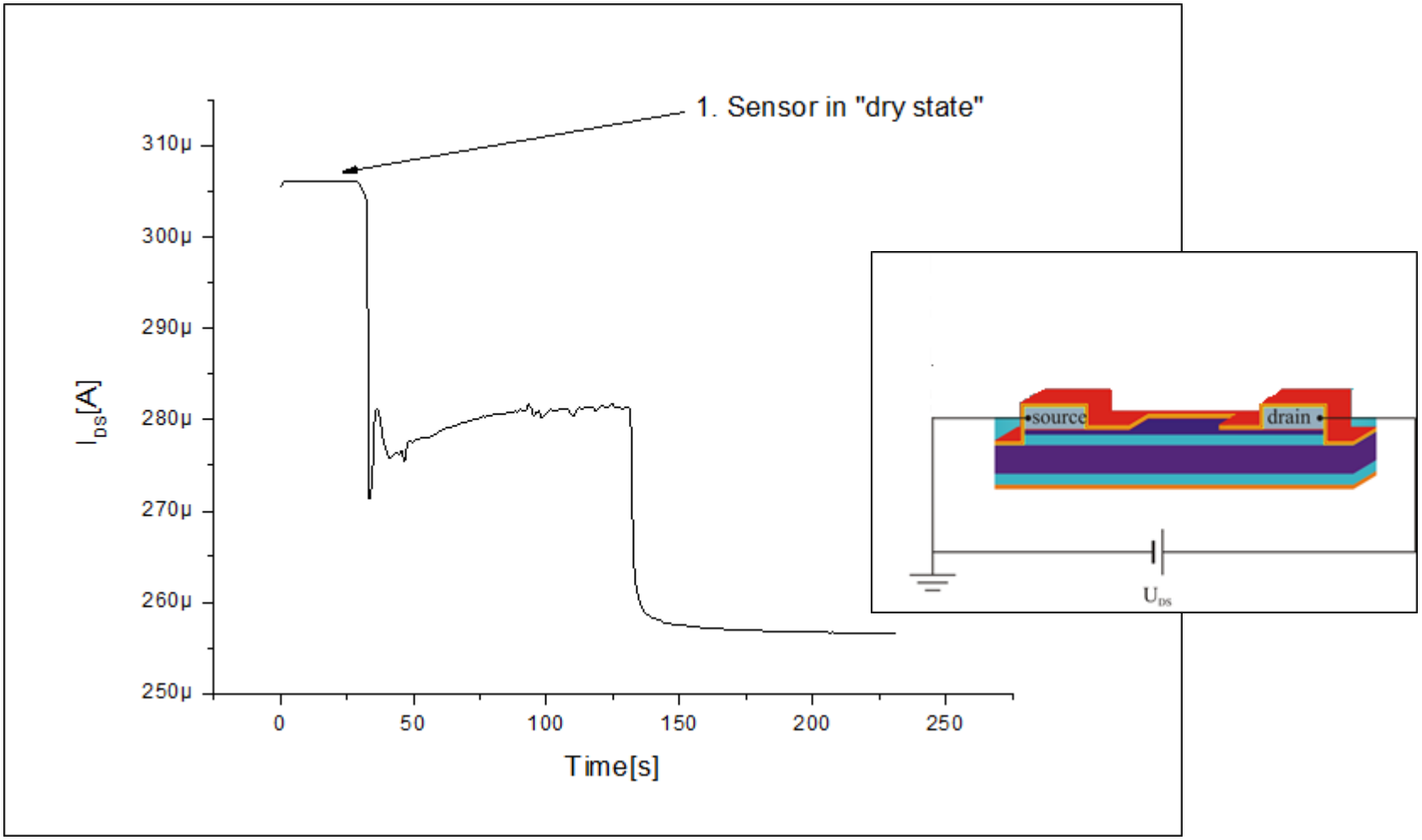
Analysis



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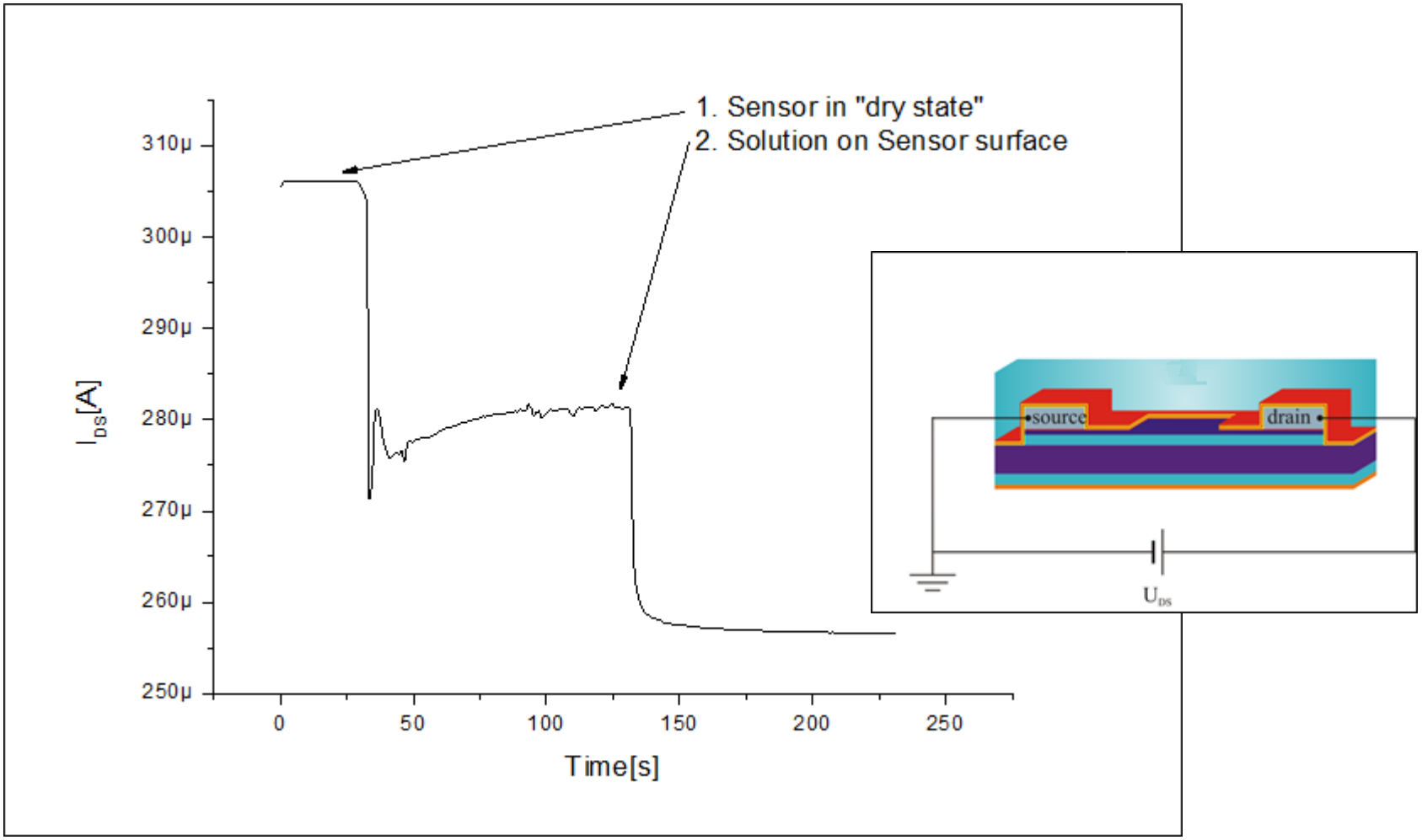

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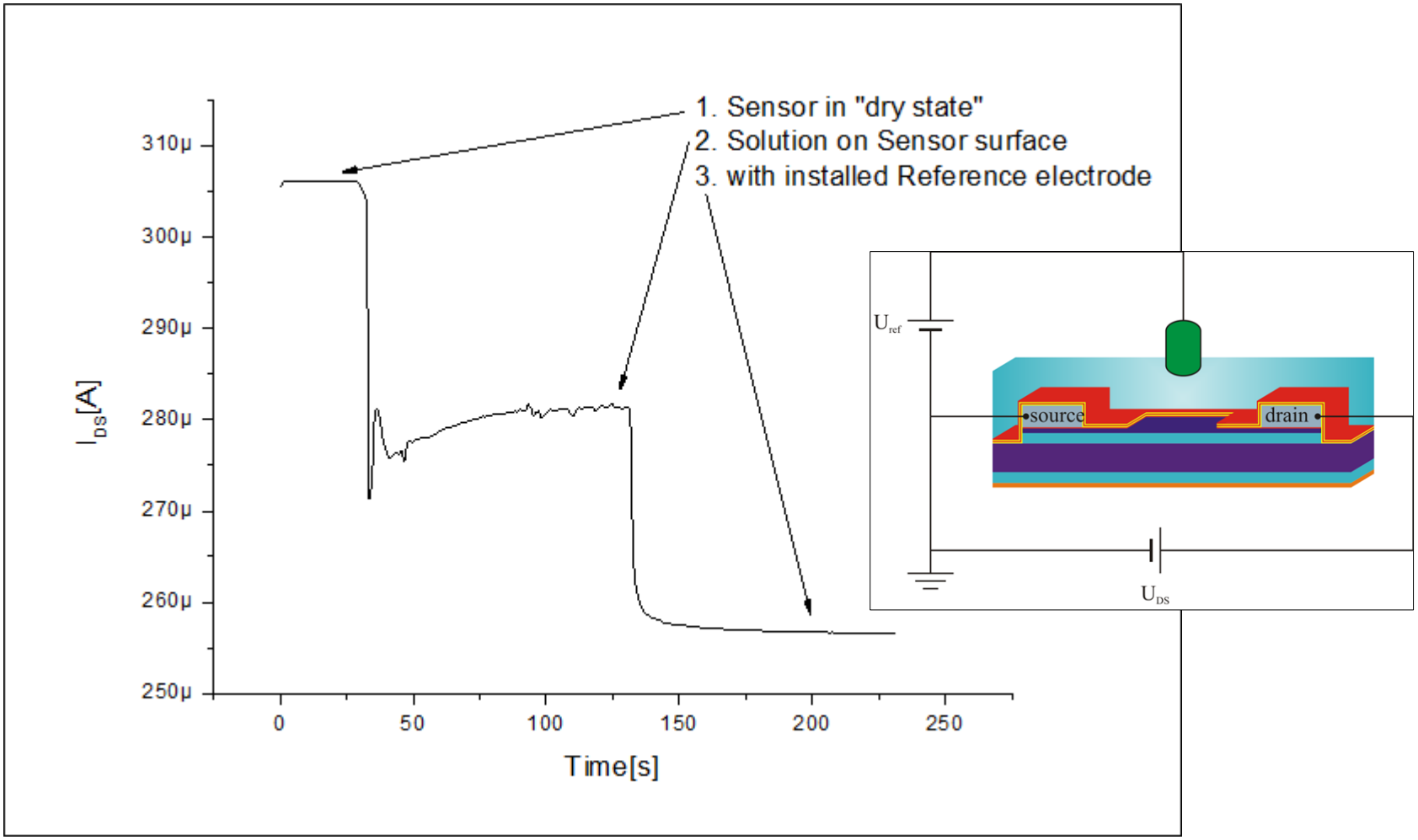

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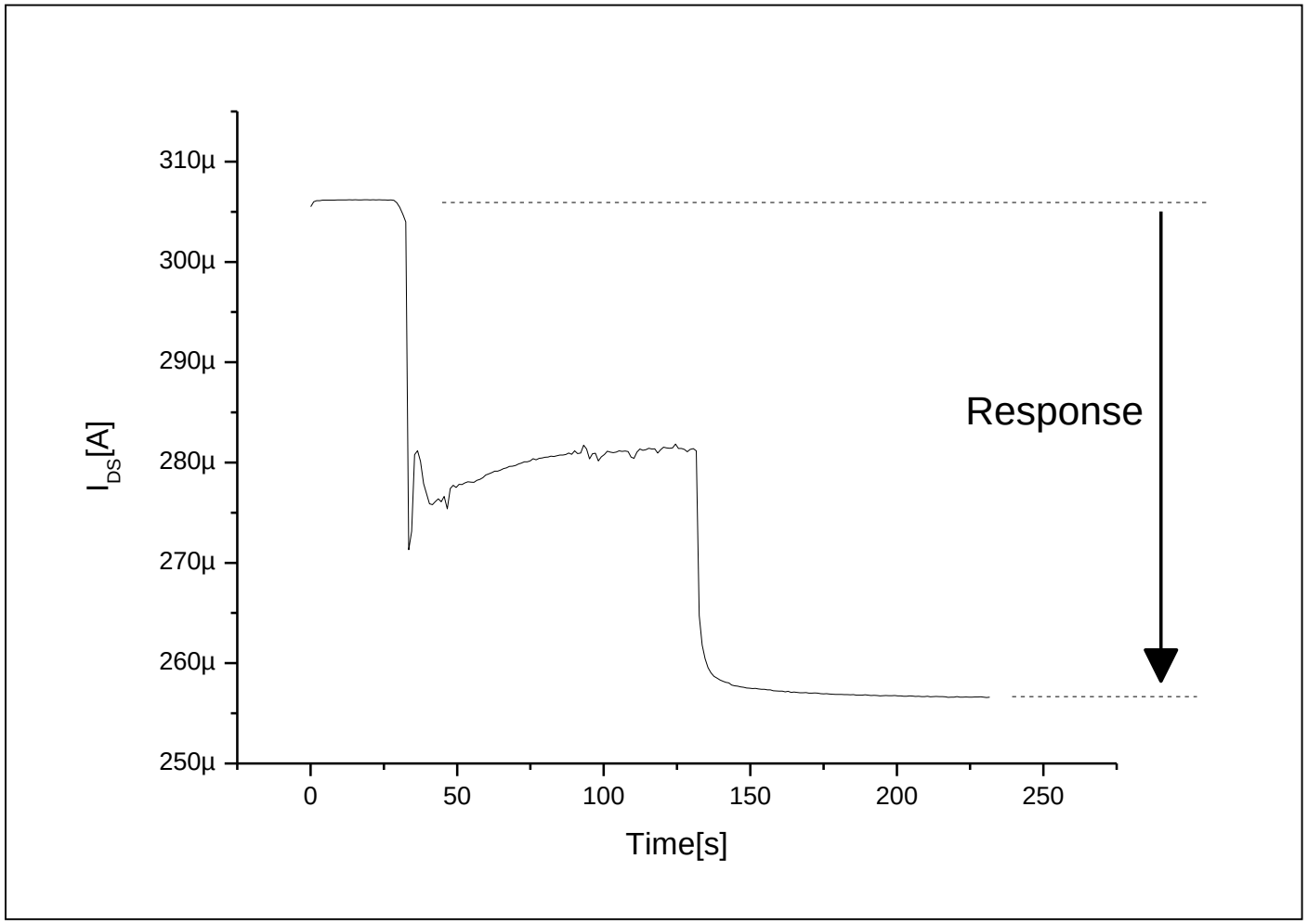

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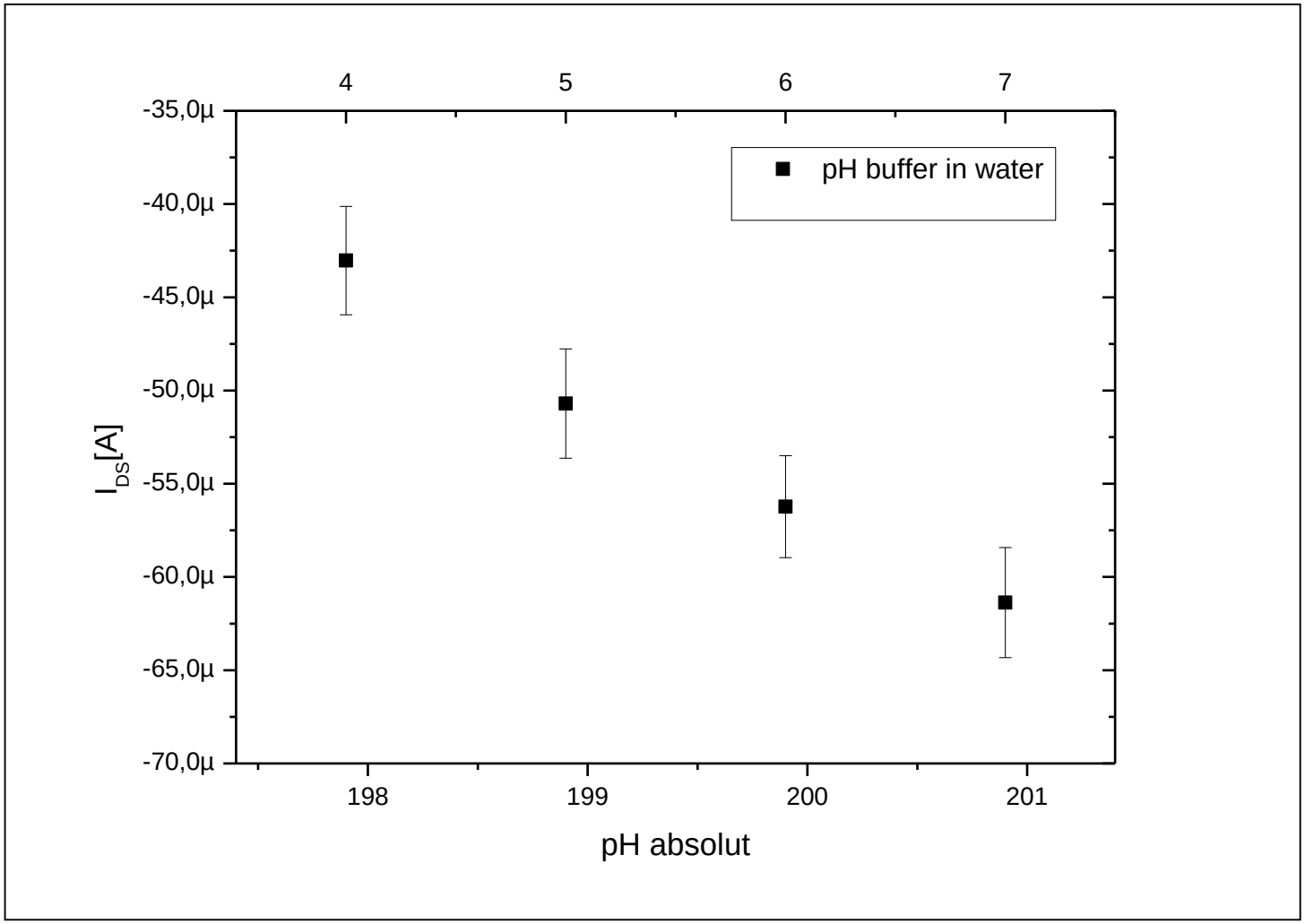
Results



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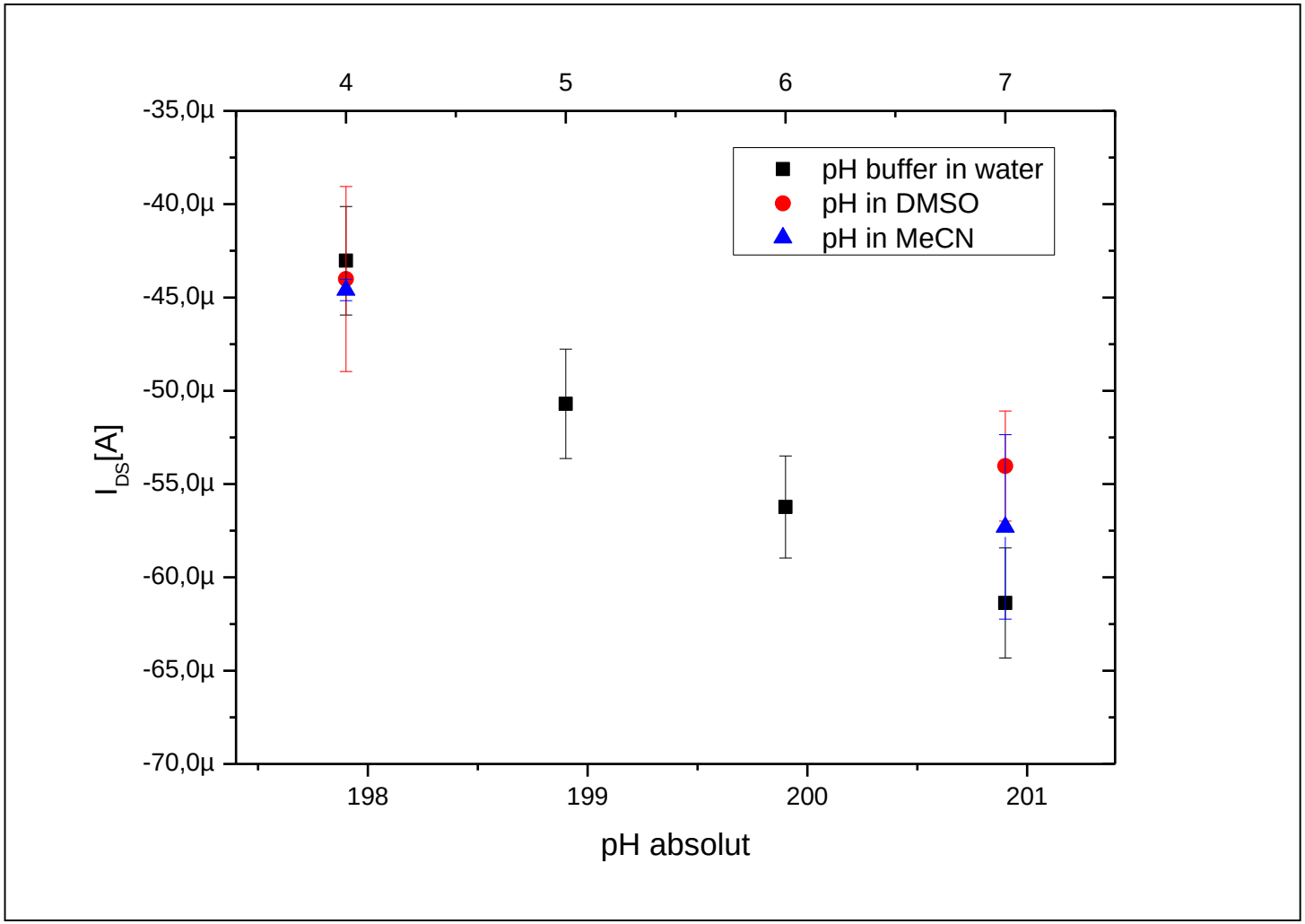

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Conclusions

- Unified pH-scale
- Calibration in water based buffers

- Future work:
  - Investigate on solvent influence

Thank you for your attention!