Exploring the Feasibility to make a "Paint Battery"

Andreas Grasser, 26.06.2021

Motivation

- Battery production has many steps

→In-situ production often impossible

→More steps → more expensive

Final goal

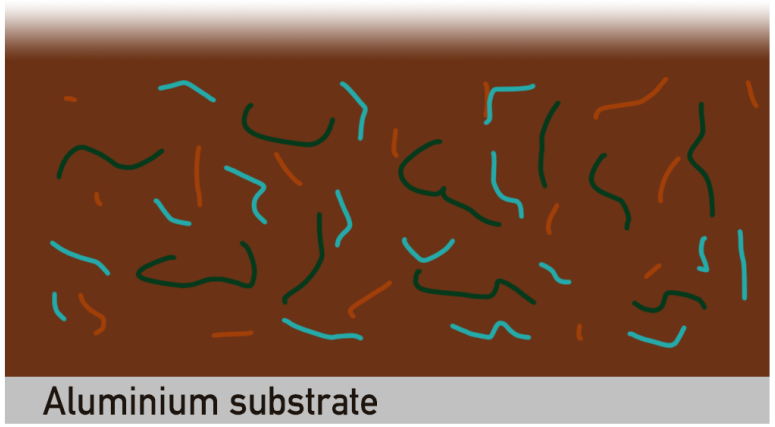
- One paint that produces the three layers of a battery by itself:
  - cathode
  - gel electrolyte / seperator
  - anode

- “Wall paint that forms a battery”

https://www.obi.de

Final goal

1. Casting of the substrate with paint



Possible steps

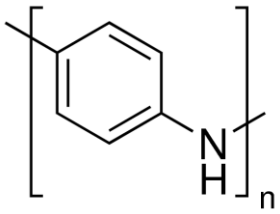
- Solvability experiments with the components
- Simple phase separation experiments
- Manually assembled battery using spin-coating etc. for benchmark
- “Hybrid” battery with self-stratification of two layers + one spin-coated layer
- Complete battery using self stratification
- Further improvements

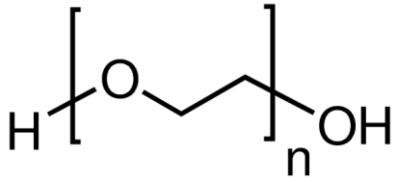
Reality: not that straight forward

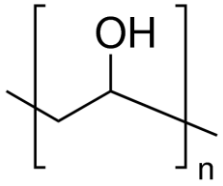
Final goal

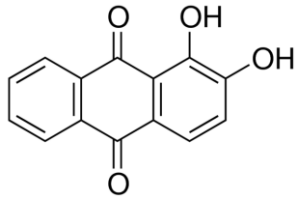
Main material focus:

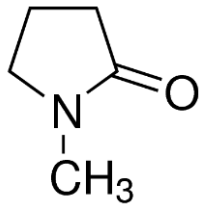
- Polyaniline (PANI)
- Polyethylene glycol (PEG)
- Polyvinyl alcohol (PVA)
- Alizarin
- N-Methyl-2-pyrrolidone (NMP)





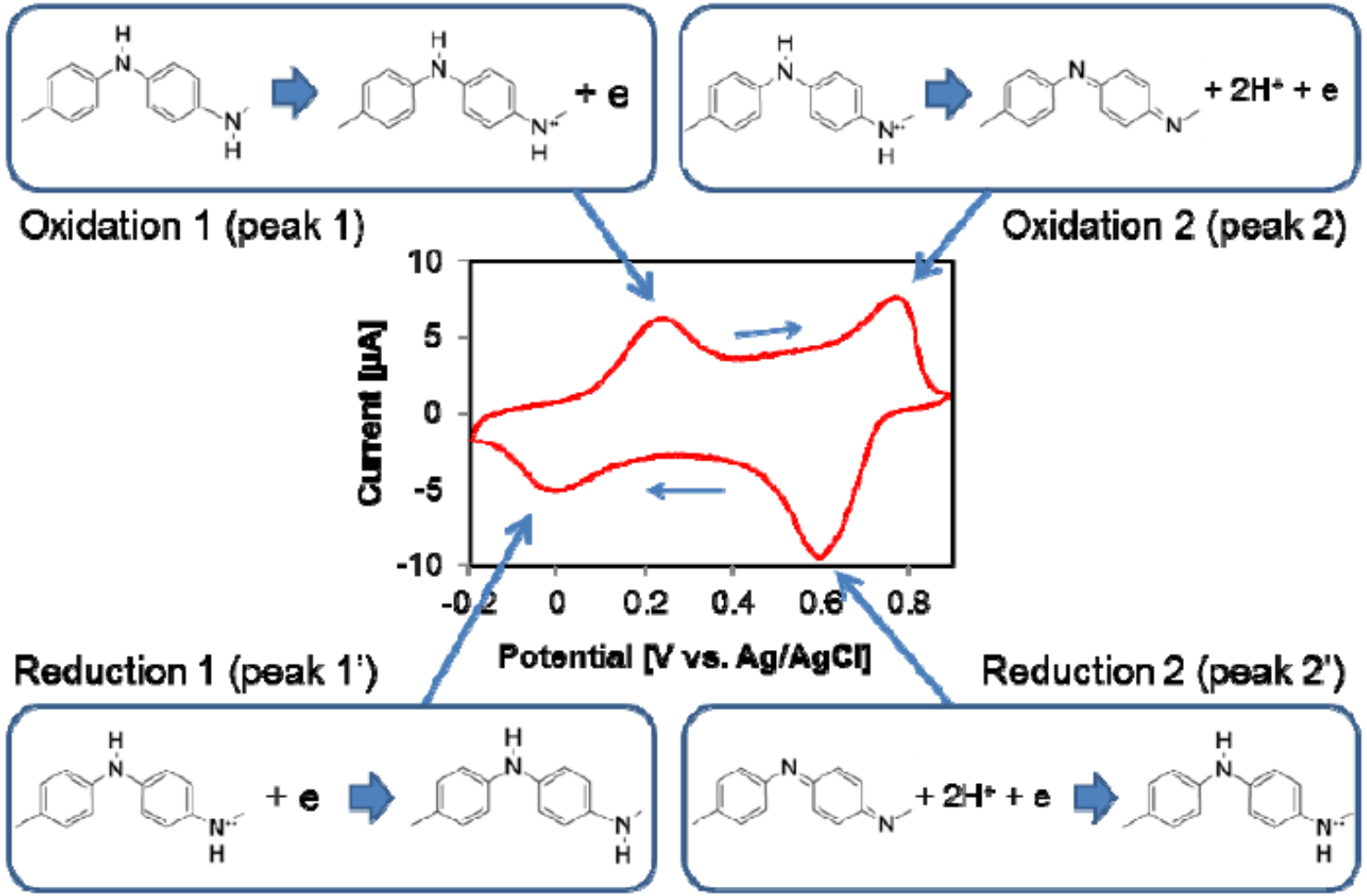






https://www.sigmaaldrich.com

Polyaniline reduction / oxidation



Song, Edward & Choi, Jin-Woo. (2013). Conducting Polyaniline Nanowire and Its Applications in Chemiresistive Sensing. Nanomaterials. 3. 498-523. 10.3390/nano3030498.

Solvability experiments

- One solvent needed for all three polymers
- Bottleneck in solvability: PANI
- Experiment: PANI with different solvents and different treatments

→ NMP as a good candidate

Solvent has influence on stratification process

Also: PANI with shorter chain length better

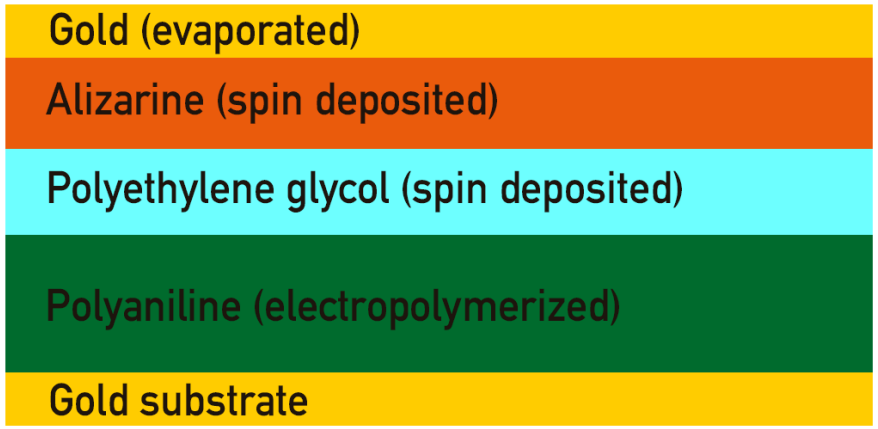
Manual Battery

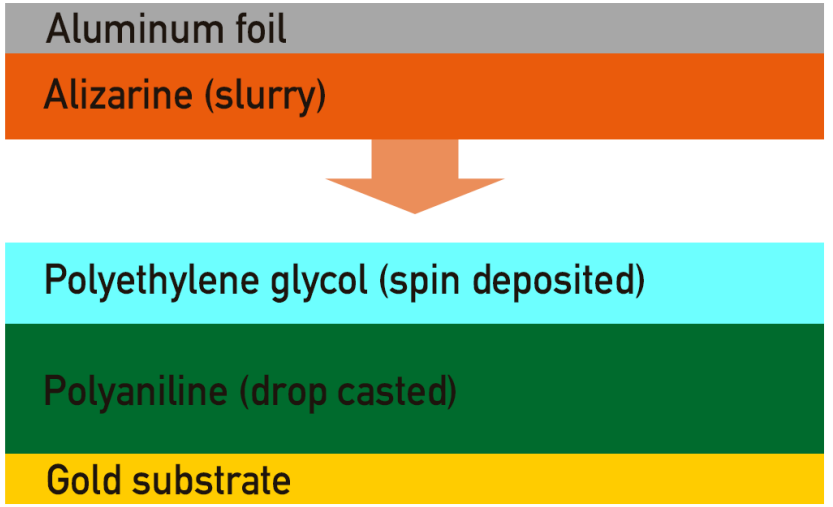
- Creating the layers of the battery without self-stratification
- Using well-known techniques for battery fabrication

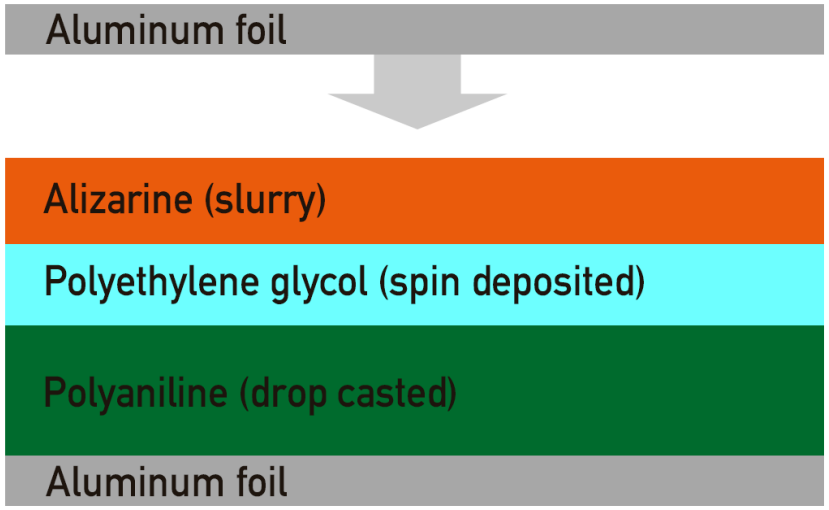
→Benchmark for the final battery

→Allows to move stepwise towards a complete self stratifying battery

Manual Battery





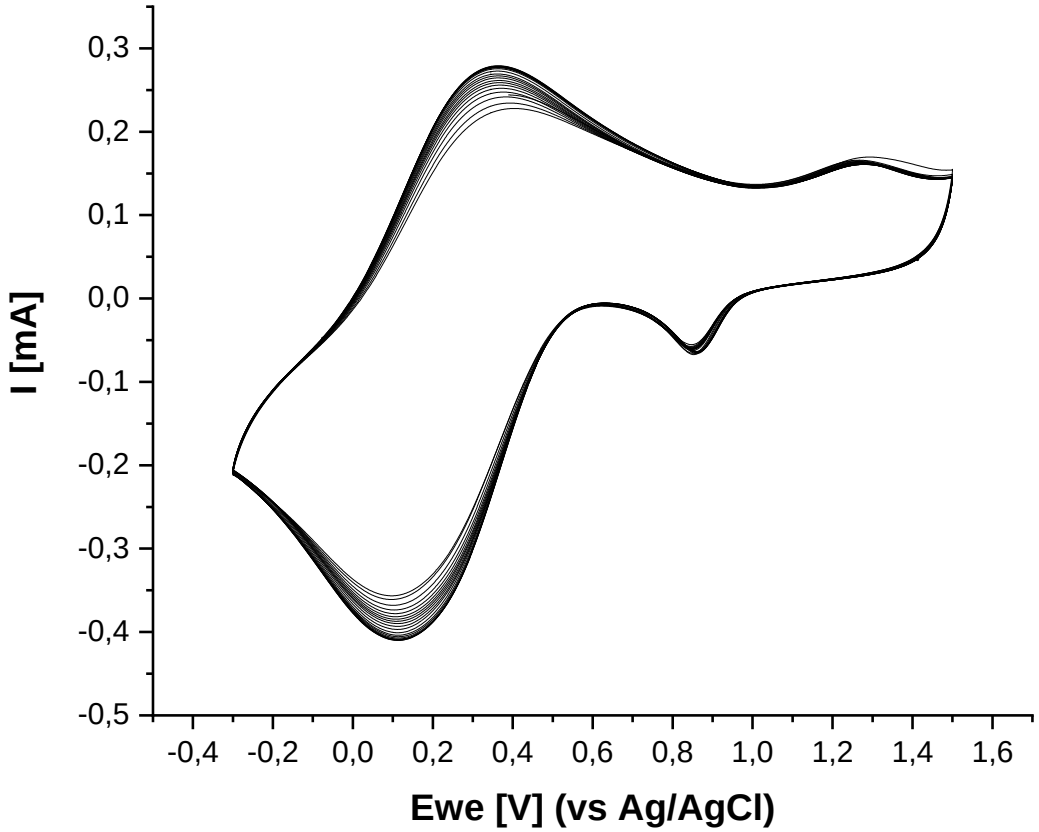


Manual Battery

Problem: Electropolymerisation of PANI on metal surfaces did not work

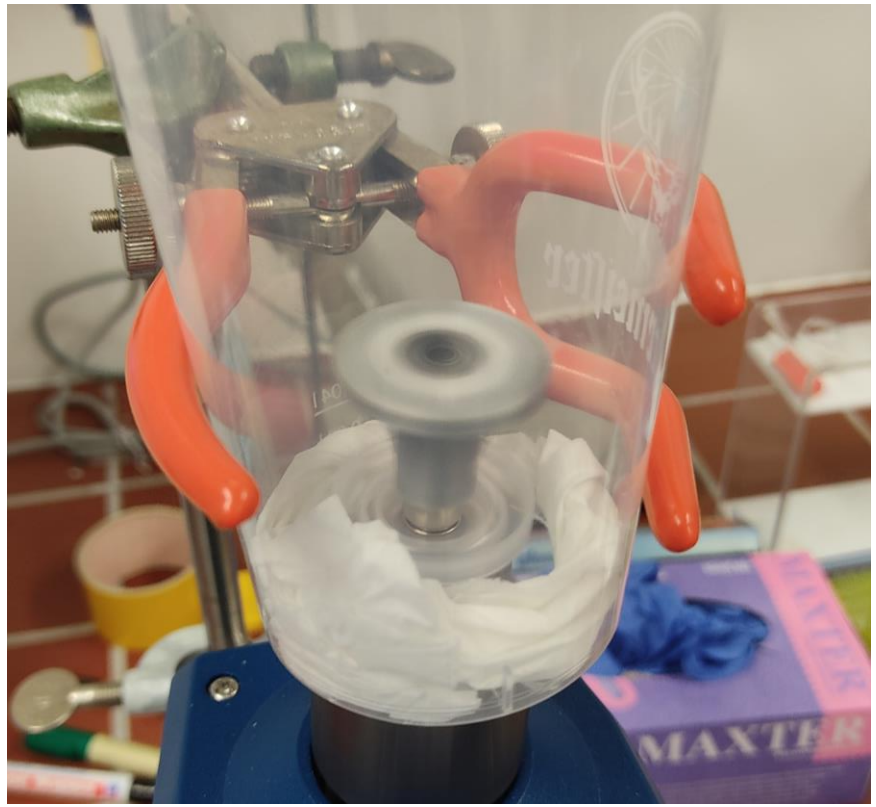
Can one dropcast PANI instead of electropolymerize it?

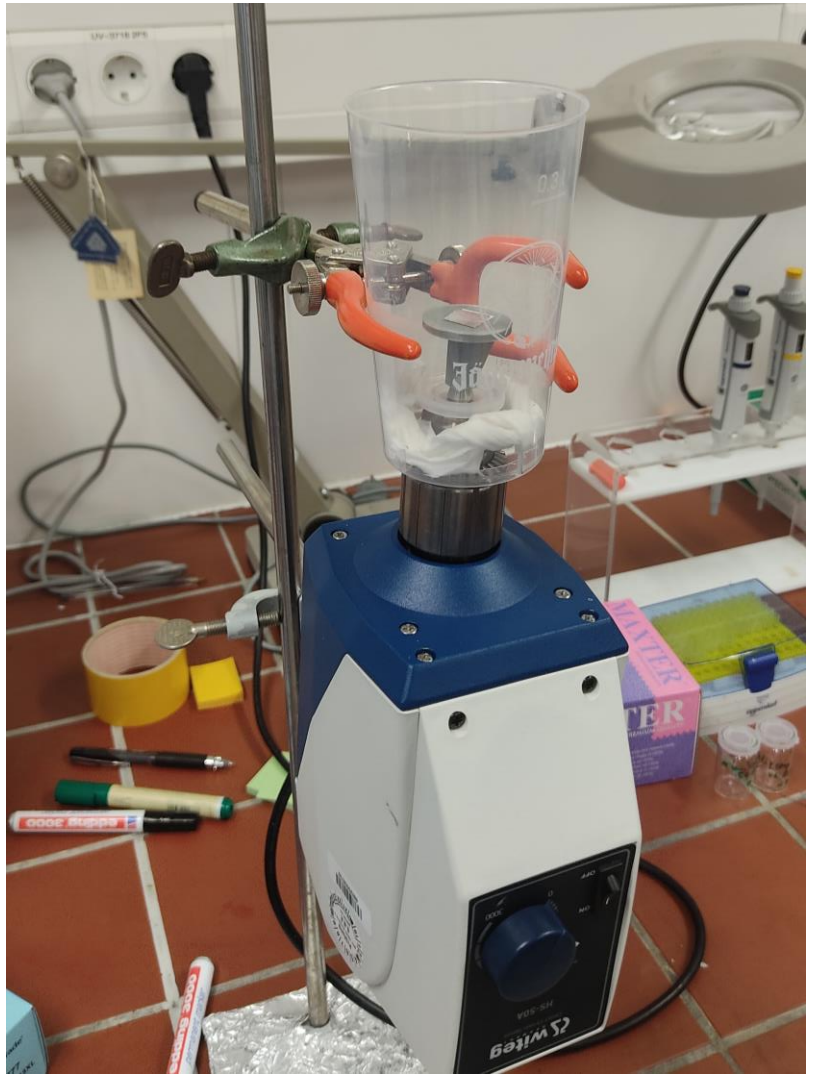
→ CV of drop casted PANI (in 8M $NaClO_4$)



Manual Battery

- Using DIY 3D-printed spin coater





Contact angle measurements

- Measure hydrophility of surface

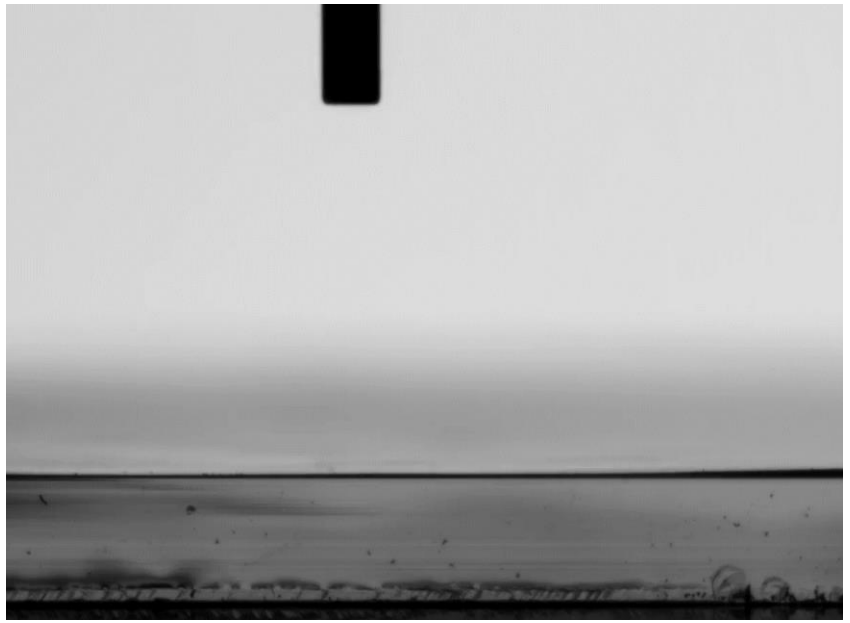
→ possible test for a successful stratification

→ with different liquids: measurement of free surface energy possible

+ Very fast and easy

- Many error sources

  (soaking into PANI, dirt on surface, different film thickness, …)

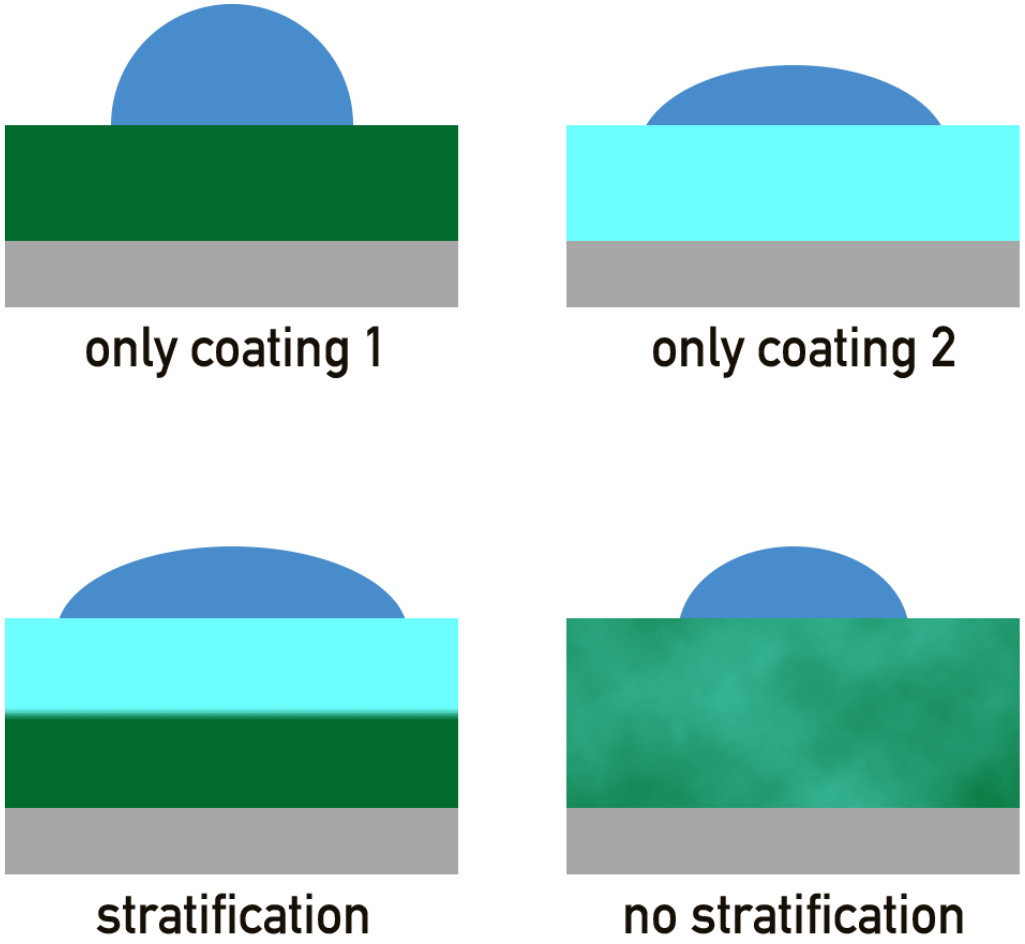


Contact angle measurements

- Compare contact angle of different samples:
  - Polyaniline
  - PVA/PEG
  - Polyaniline + PVA/PEG

- For a successful stratification:
  contact angle of mixture should show strong tendency towards one of the single components

Contact angle measurements



The self-statification process

- Driving forces for self-stratification:
  - Gravity
  - Selective wetting mechanism
  - Pigment wetting mechanism
  - Surface tension gradients
  - Phase contraction
- Two models for predicting self-stratification:
  - UNIFAC model
  - Surface energy based model

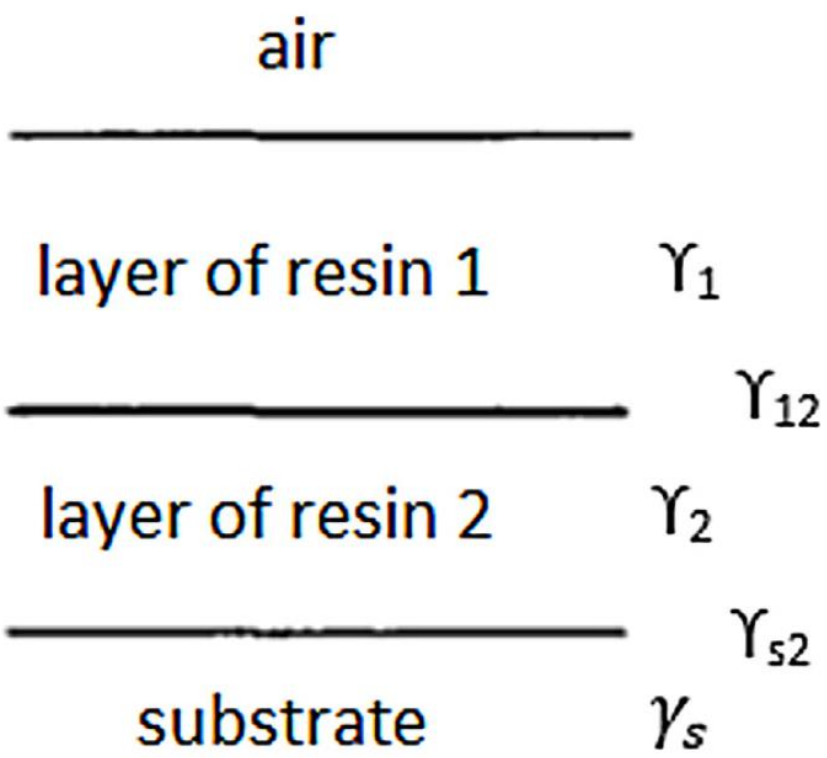
The surface energy based model

- Assumptions:
  - Surface free energy is main driving force of stratification
  - Solvent has no influence in stratification

+ Relatively easy to measure and calculate

- Even in an advanced form no perfect prediction possible

The surface energy based model



3 conditions:

$$\gamma_{s1} \geq \gamma_{s2} + \gamma_{12}$$

$$\gamma_{s1} + \gamma_2 > \gamma_{s2} - \gamma_1$$

$$\gamma_s > \gamma_{s2} + \gamma_{12} + \gamma_1$$

Christopher Carr, Eva Wallstöm, Theoretical aspects of self-stratification (1996)
https://doi.org/10.1016/0300-9440(95)00594-3

The surface energy based model

- Possibility to estimate interfacial surface tension from surface energies:

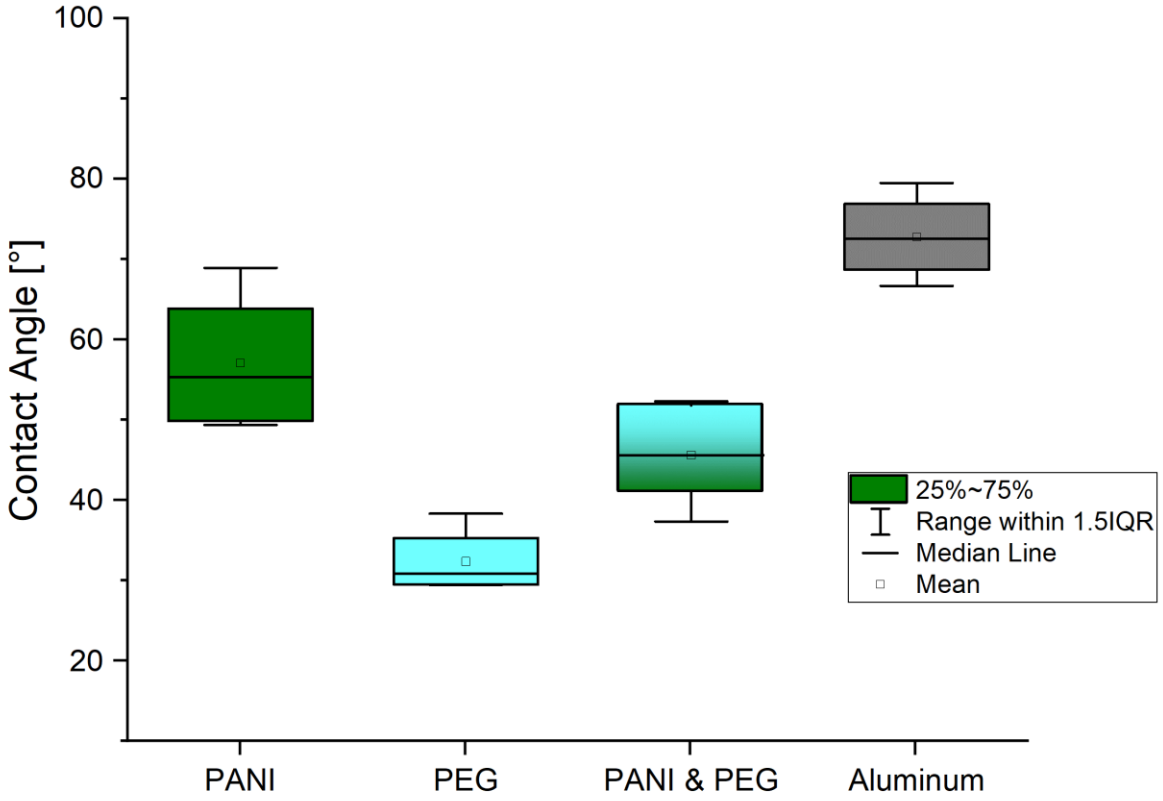
$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4 \cdot \gamma_1^d \cdot \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4 \cdot \gamma_1^p \cdot \gamma_2^p}{\gamma_1^p + \gamma_2^p}$$

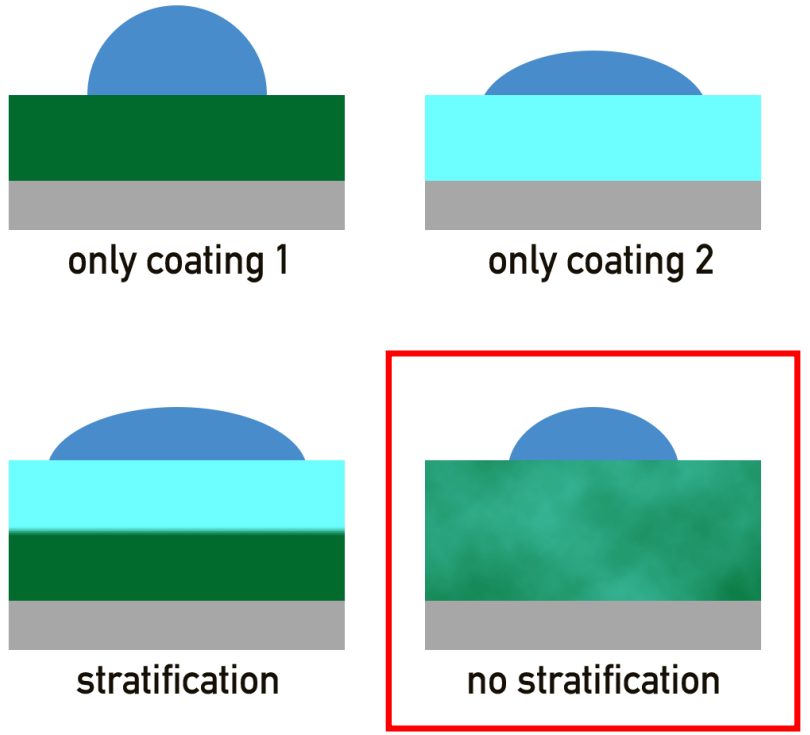
$\gamma_{1,2}^d$: dispersive component of surface free energy

$\gamma_{1,2}^p$: polar component of surface free energy

Battery with two layer stratification

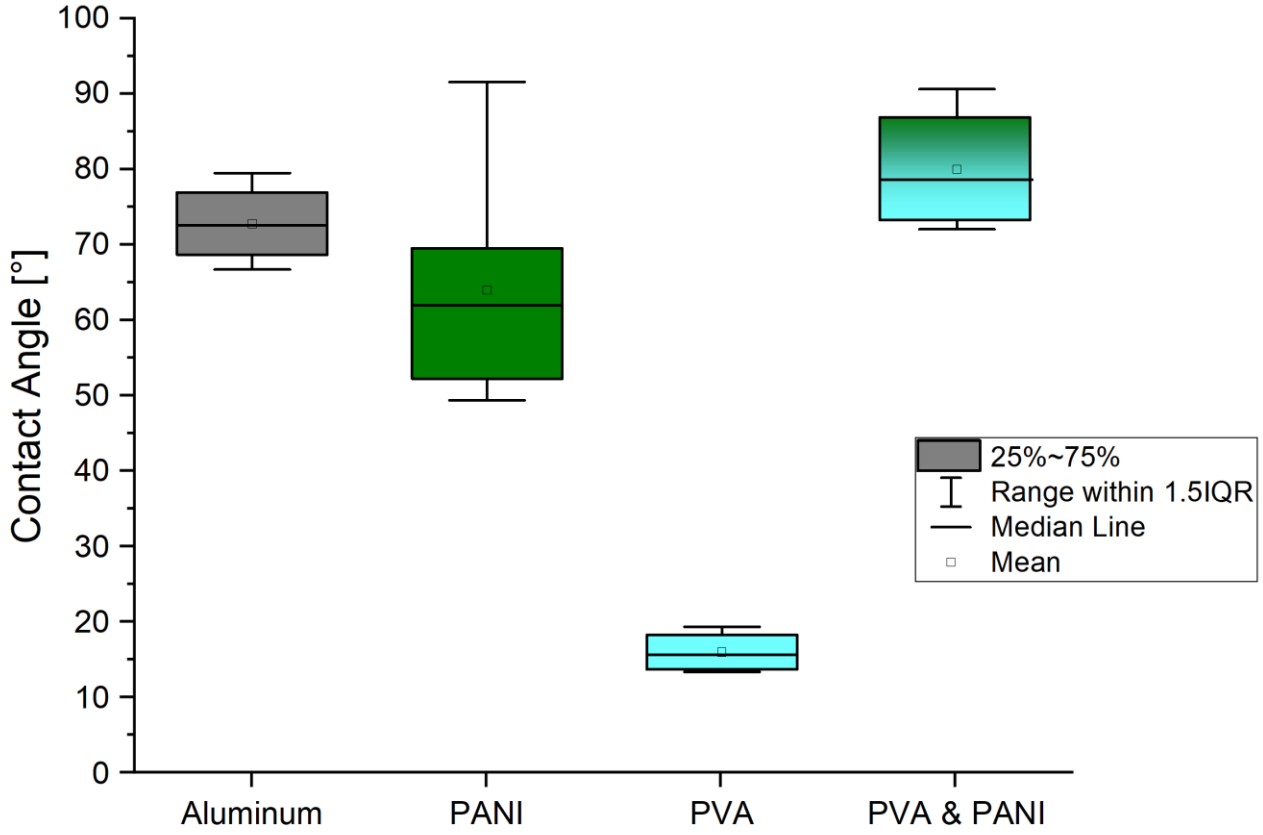
- No stratification signs for PEG

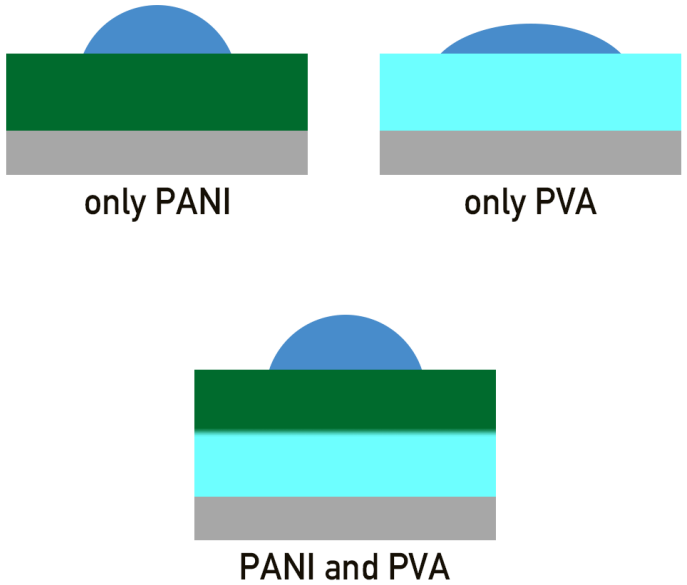




Battery with two layer stratification

- Stratification of Polyaniline + PVA on Aluminum foil?



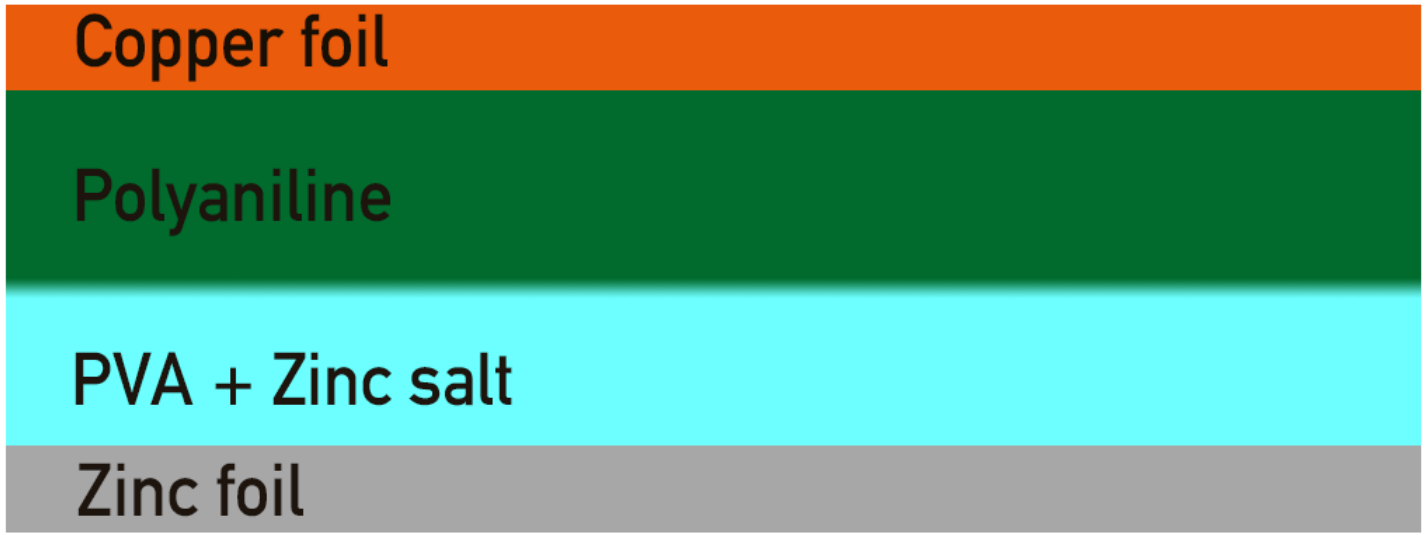


Battery with two layer stratification

- Big problem: how to add third layer beneath the coating?
- Using a zinc surface as anode and Zinc Perchlorate as conducting salt
- Difficulties:
  - Zinc has different surface energy than Aluminum
  - Zn^{2+} /Cl^{-} instead of Na^{+} ions

Battery with two layer stratification

- First test with copper current collector gave a voltage of ~0.6V
  (Reaction directly between zinc ions and copper foil?)

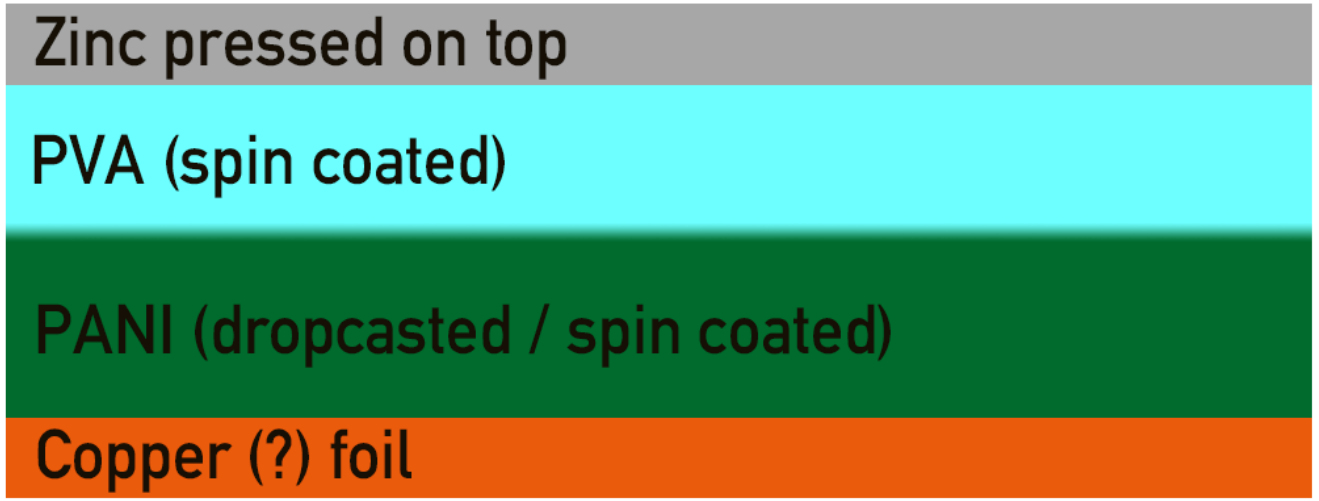


Manual zinc battery

- PVA easily solvable in NMP

Spincoating of PANI on top of PVA not possible

- Building the battery bottom up



Ways to do three layer stratification

- Try stratification by free surface energy mechanism

→ Not many three-layer stratifications reported in the literature

→ Complete & reliable stratification is necessary (short circuits!)

- Using a magnetic third component to force stratification

- …?

Further plan

- Build a complete working manual zinc based battery
- Determine the surface free energy of the coatings
- Use elipsomerty to do advanced testing for self-stratification