Unveiling Mechanistic Differences in the Curing of Copper and Silver Pastes for Heterojunction Solar Cells

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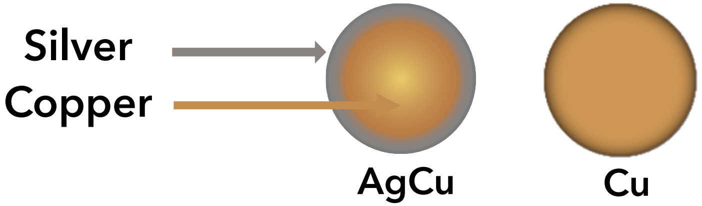
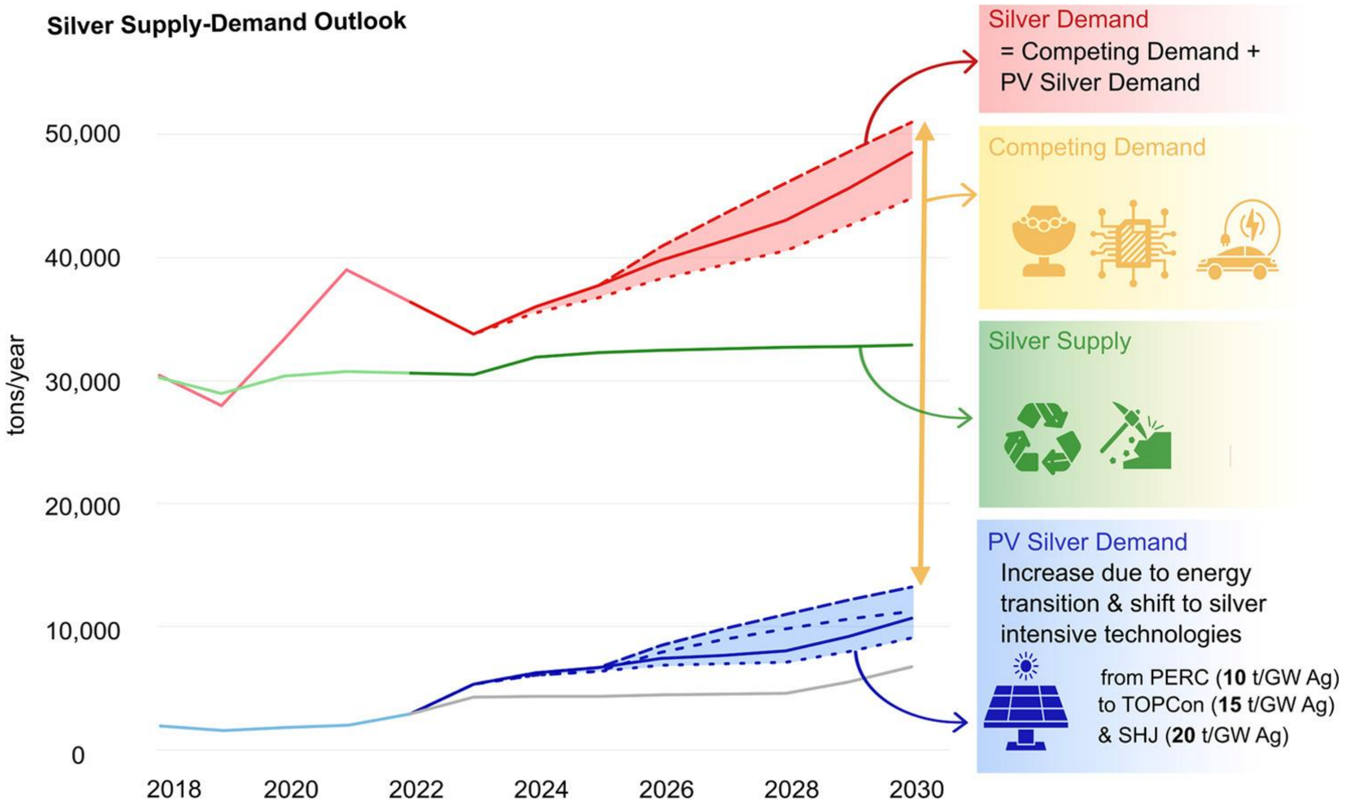
Motivation

Silver high demand

- Today: 5 mg/W (PERC) – 17 (9) mg/W (SHJ) Ag is used[1,2]
- Total silver demand in 2030: 48,000 to 52,000 t/y [3]
- Growth by a factor of 1.6 to 2.3 to 10,000–14,000 t/y in 2030 ~ 29–41 % of the silver supply

⇒ Copper (1.7 µΩ·cm), as an alternative for silver





[1]Y. Chang et al., 2024, https://doi.org/10.1002/pip.3799
[2]S. Pingel. This workshop
[3]V.Cattaneo et al., https://doi.org/10.1016/j.resconrec.2025.108562

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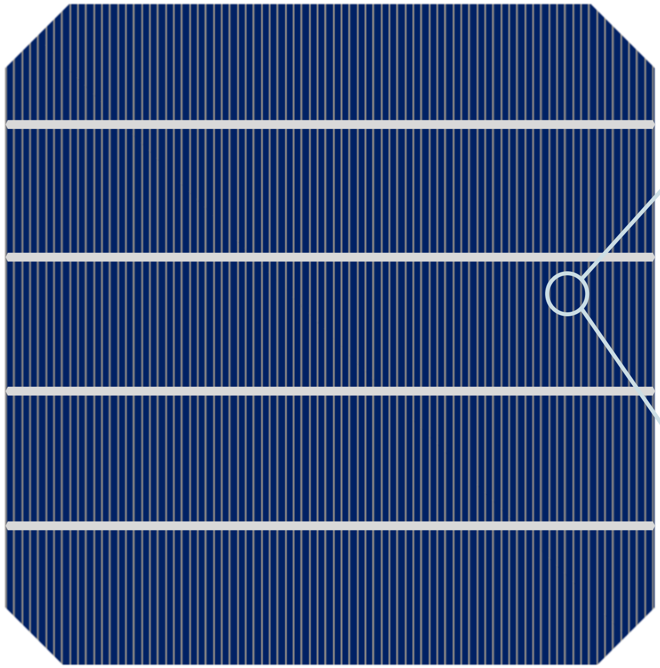
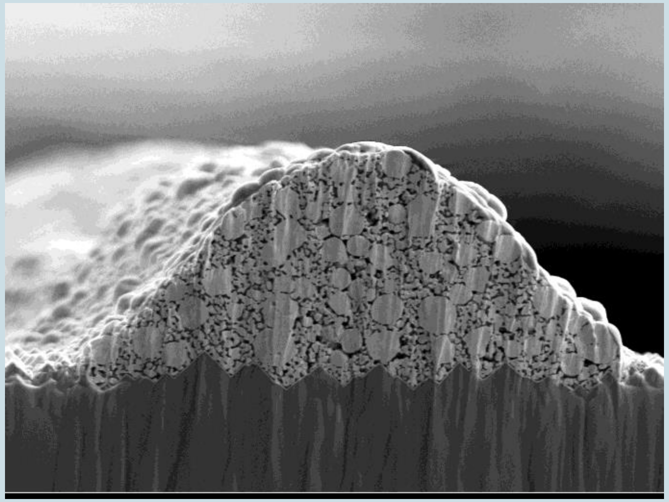
Background

Metallization: Low Temperature paste composition

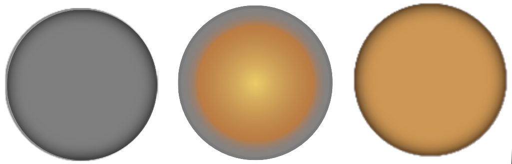


HJT Solar cell
Max. 250 °C



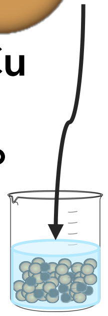
Finger post screen-printing and post curing

- Metal particles 90-95 wt%



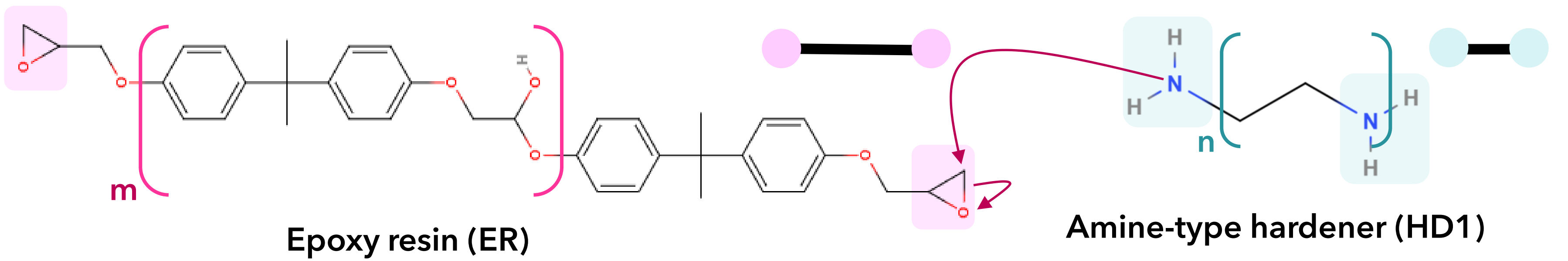
Ag AgCu Cu

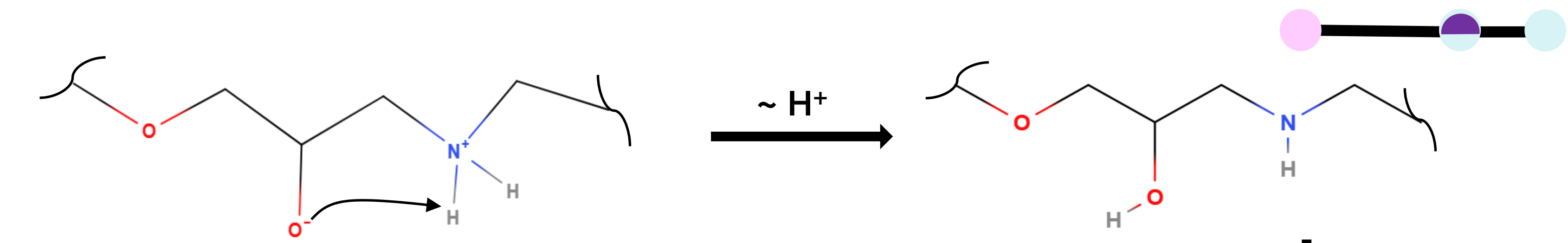
- Organics: 5-10 wt%
  - Curing system: Resin + Hardener
  - Solvents, additives

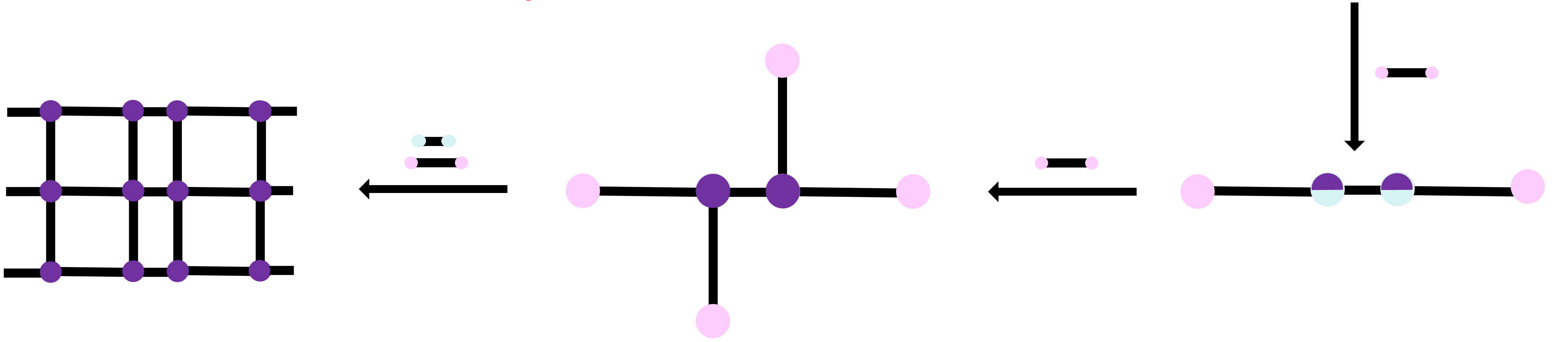


Curing mechanism

- **Why is curing important?**
  - Adhesion
  - Mechanical strength
  - Stability
- **Common curing conditions**
  - Ideally: Fast and at low temperature
  - Curing with linear primary amine
  - Nucleophilic Epoxide Ring Opening
  - Transition from liquid to solid state







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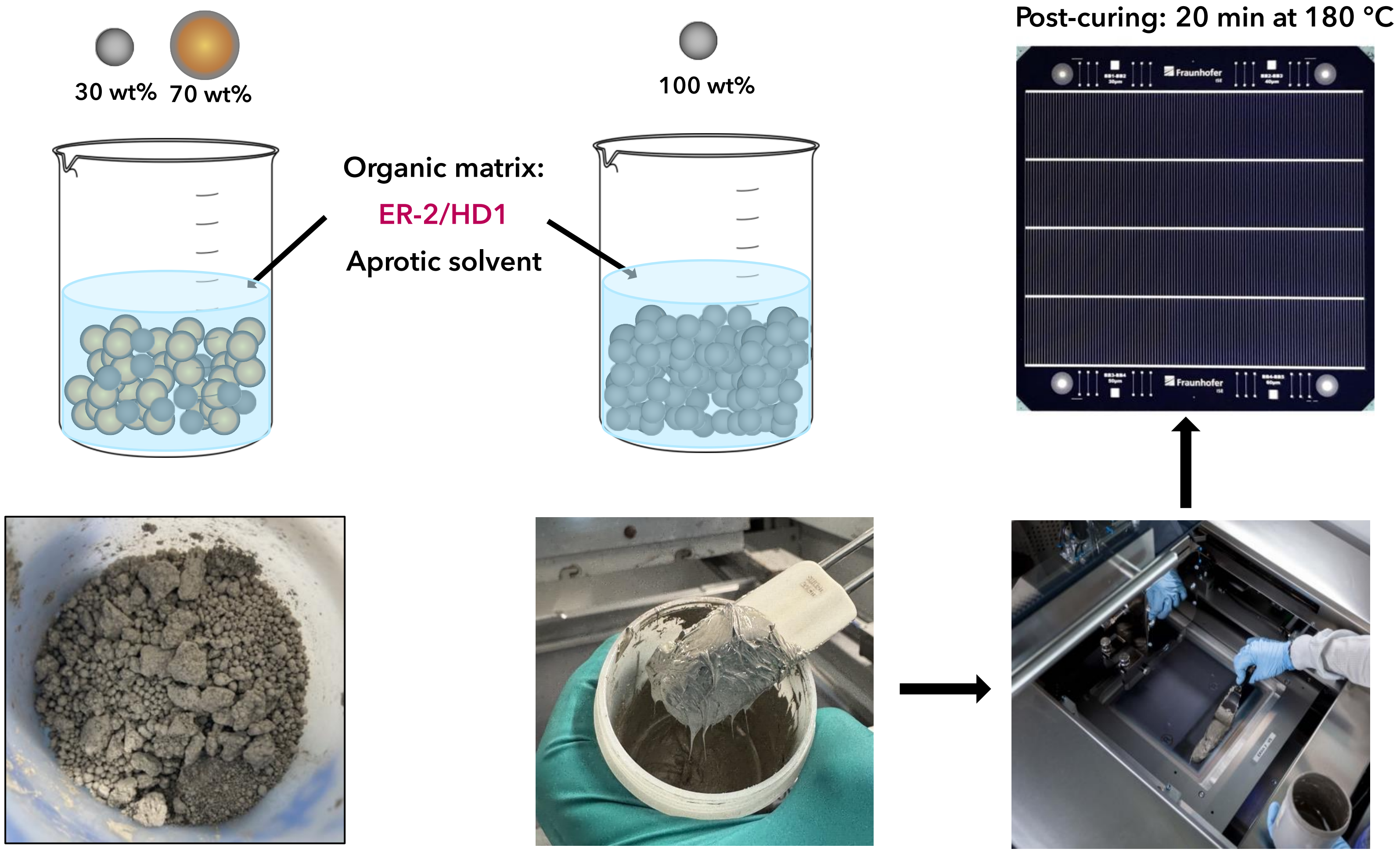
Challenges

Ag vs. AgCu

- Particle content constant 90 wt%
- Ag paste printable
- AgCu paste not printable
- Hardener-induced agglomeration
- **Why?**



AgCu paste upon incorporation of HD1

Ag paste upon incorporation of HD1

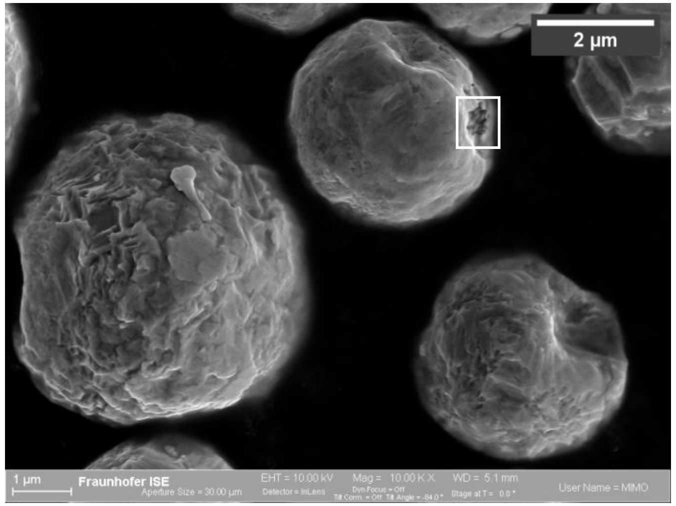
Screen Opening: 30-60 µm

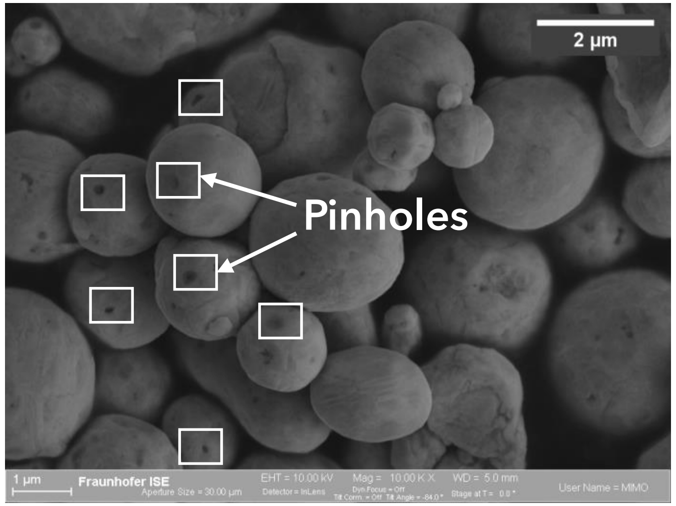
Challenges

Ag vs. AgCu

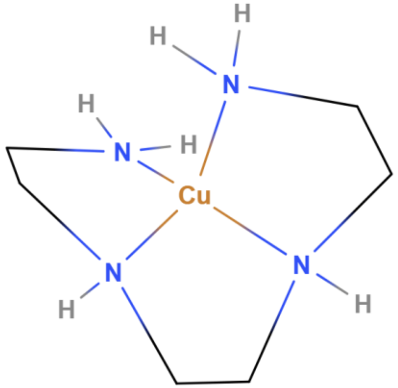
- Particle content constant
- Ag paste printable
- AgCu paste not printable
- Hardener-induced agglomeration
- **Why?**
- Non-uniform coating
- Presence of **Cu**
- Cu^{2+} in **aprotic** solvent
- Copper-amine complex

Another curing agent is required

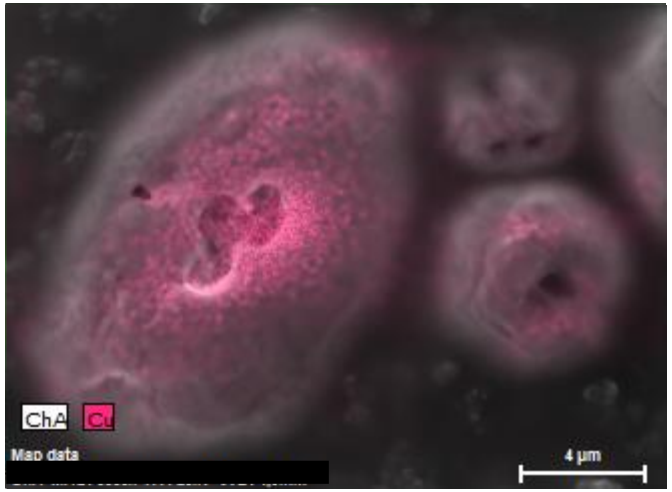




AgCu + solvent+ HD1
(Post particles filtration)



Cu^{II} (HD1)



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Curing AgCu/Cu paste

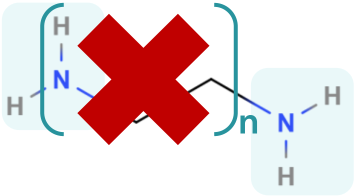
Alternative to HD1

Advantages:

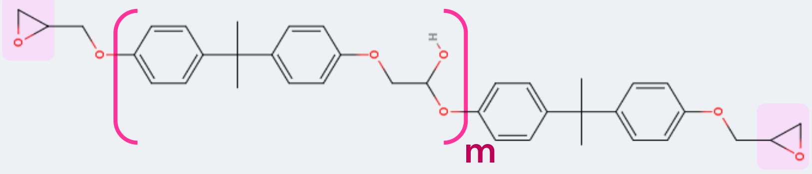
- Sterically hindered
- Latent curing agent
- Less toxic, higher T_g
- Absorb less moisture
- Reduced curing shrinkage

Mechanism:

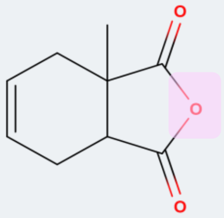
- Not nucleophilic enough
- Necessity of a catalyst



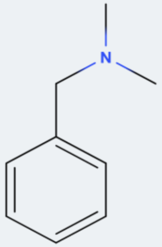
Amine-type hardener (HD1)



Epoxy resin (ER)



Anhydride-type hardener (HD2)



Catalyst (CAT)

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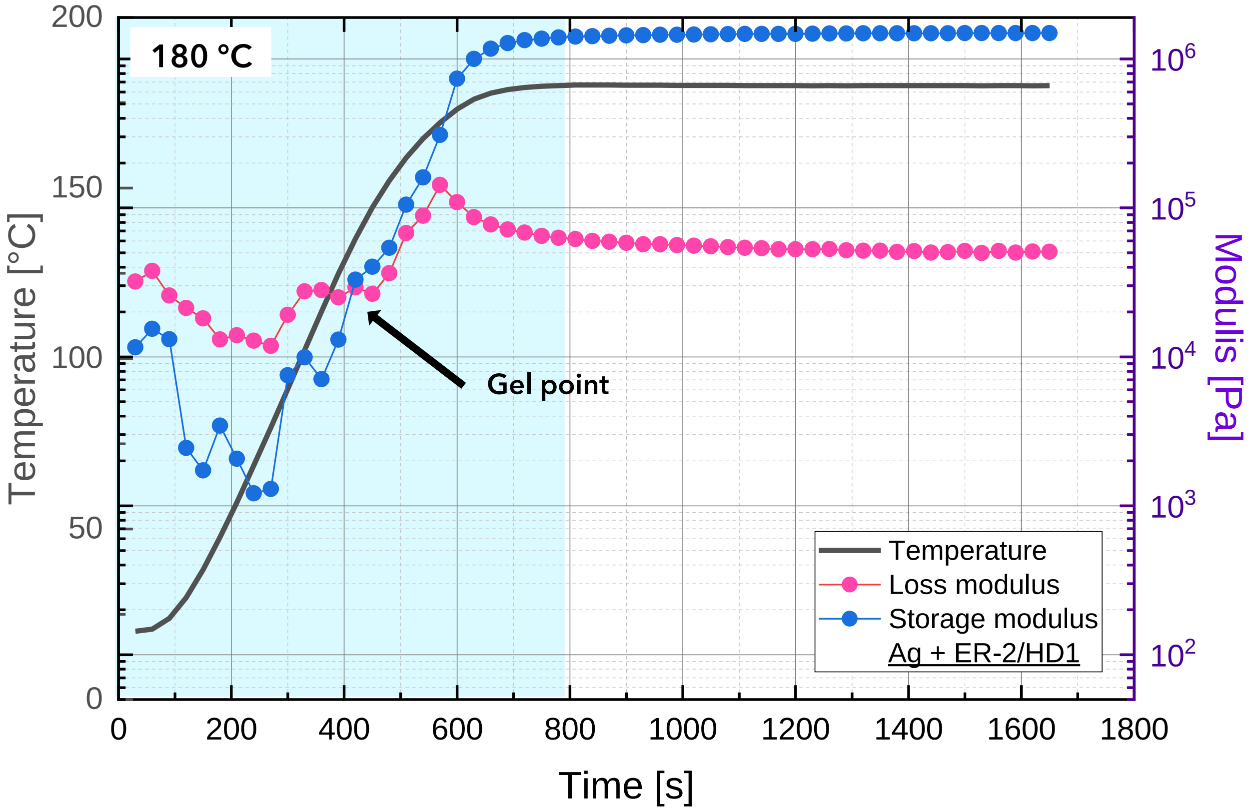
Curing with anhydride

Alternative

- **Rheological** curing profile
- Curing at 180 °C
- ω= 10 rad/s, ε = 1%
- Storage modulus: Solid state
- Loss modulus: Liquid state

Paste	Curing time [min]
Ag + ER-2/HD1	11
Ag + ER-2/HD2/CAT	17
AgCu + ER-2/HD2/CAT	20
Commercial paste (CP)	6



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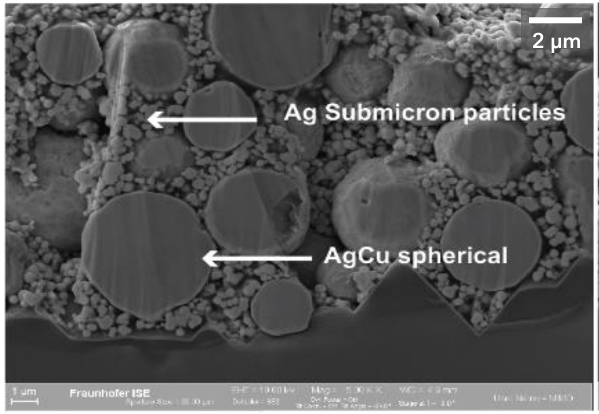
Curing with anhydride

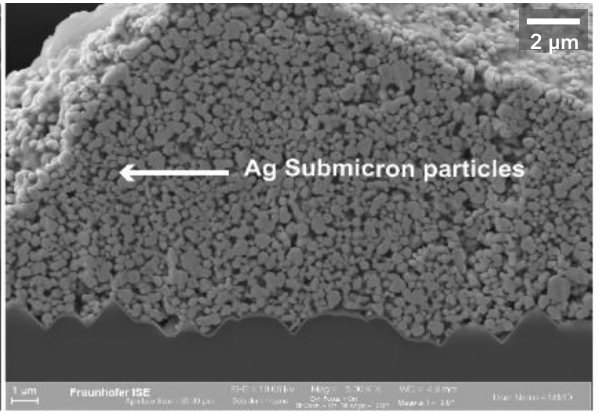
Alternative

- Rheological curing profile
- Curing at 180 °C
- Solvent entrapment for Ag+ ER-2/HD1
- Small silver particles catalyze the reaction

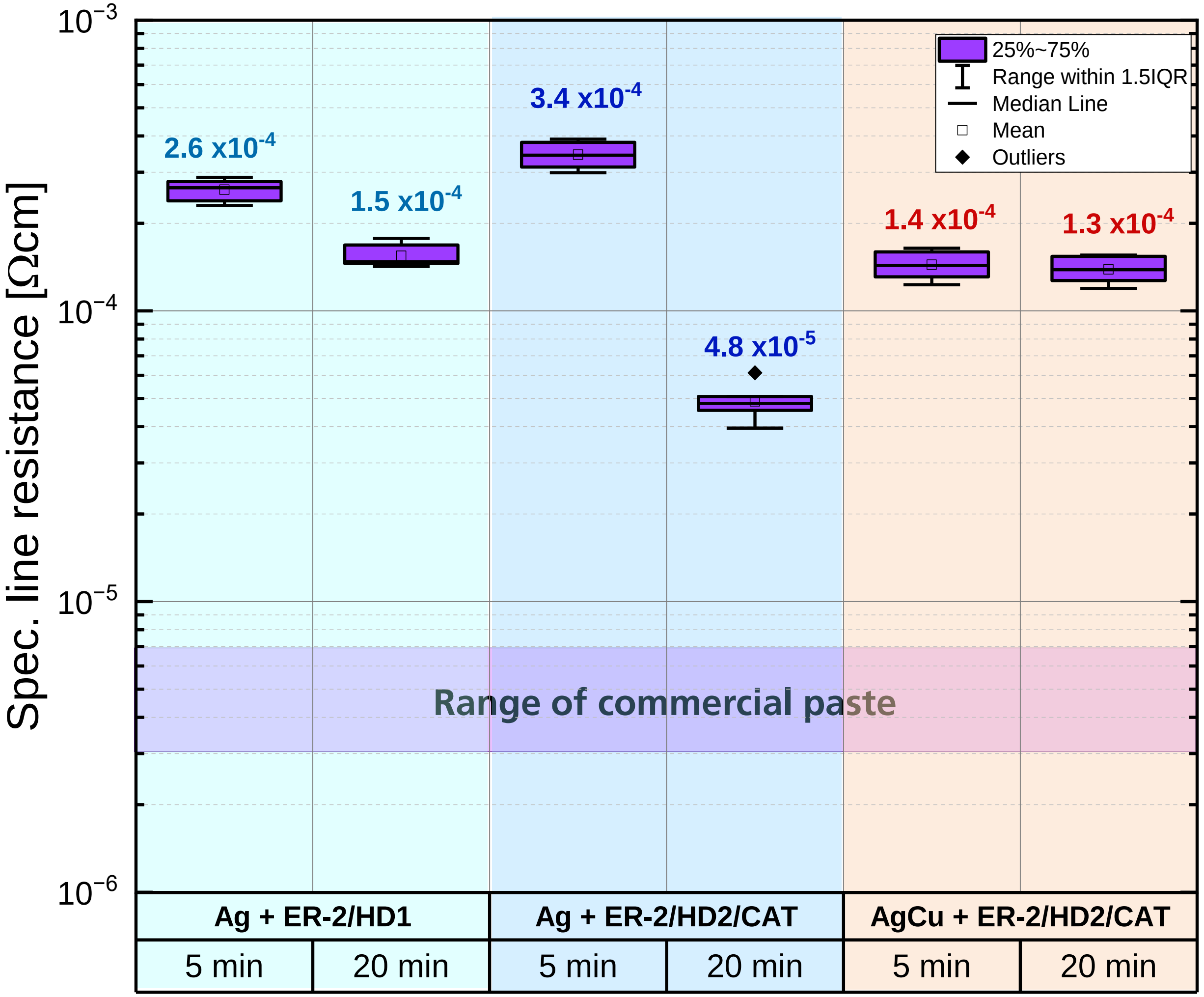
Paste	Curing time [min]
Ag + ER-2/HD1	11
Ag + ER-2/HD2/CAT	17
AgCu + ER-2/HD2/CAT	20
Commercial paste (CP)	6



AgCu-Paste



Ag-Paste



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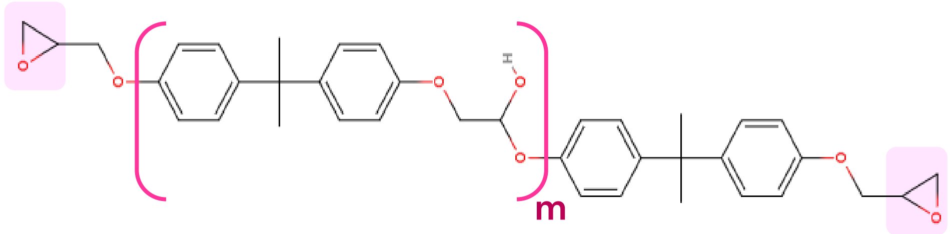
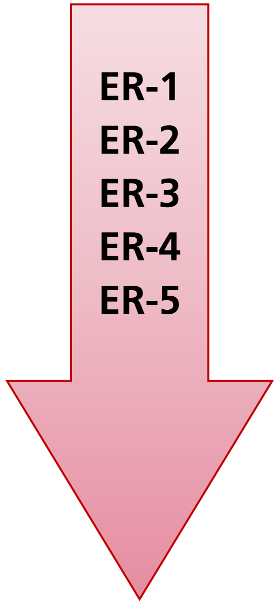
Variation of epoxy resins (ERs)

Alternative

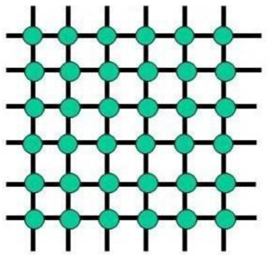


- **Varying the repeating unit m and its impact on:**
  - Curing rate
  - Adhesion
  - Line resistance
- => **5 Pastes with Epoxy Resins PER:**
  PER-1 (low MW) → PER-5 (high MW)

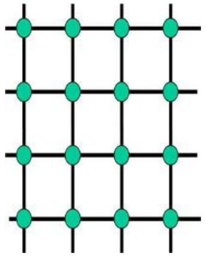


Increasing the chain length (m)

Type of crosslinking



High T_g, Solvent resistance
Tendency to brittleness



High fracture toughness
Flexibility

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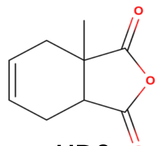
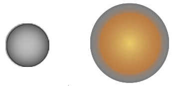
Variation of epoxy resins (ERs)

Alternative



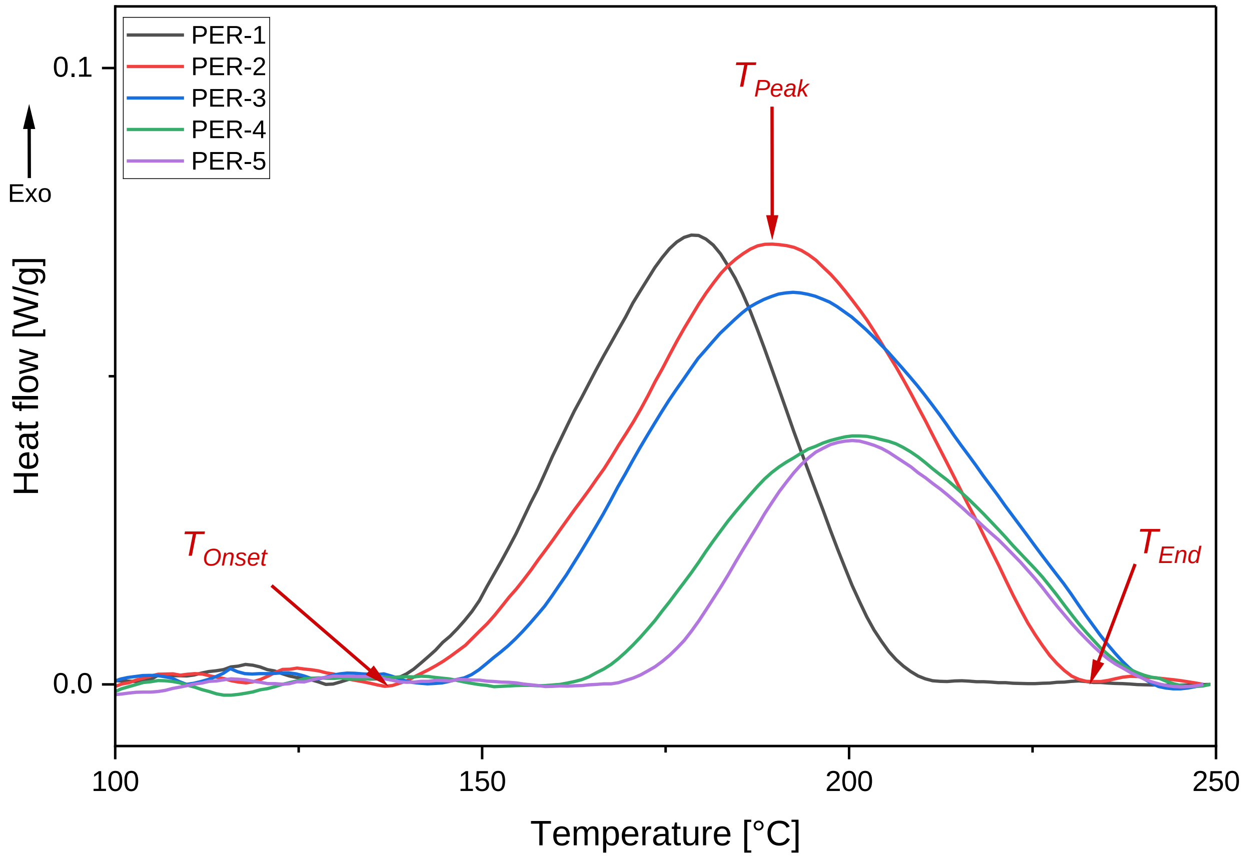
HD2



30 wt% 70 wt%

- **5 Pastes with Epoxy Resins PER:**
  PER-1 (low MW) → PER-5 (high MW)
  - Curing system 10 wt%
  - Metal content 90 wt%
- **Differential Scanning Calorimetry (DSC)**
  - Heating rate: 10 °C/min
  - Exothermic peak => Curing peak
  - => **PER-1** fastest

Paste ID	T_{Onset} [°C]	T_{Peak} [°C]	T_{End} [°C]	Heat released [J/g]	Residual Heat [J/g]	Curing degree
PER-1	132	179	211	29	15	65%
PER-2	143	191	232	19	12	62%
PER-3	147	193	240	19	17	53%
PER-4	161	200	241	11	16	40%
PER-5	170	201	242	9	18	34%



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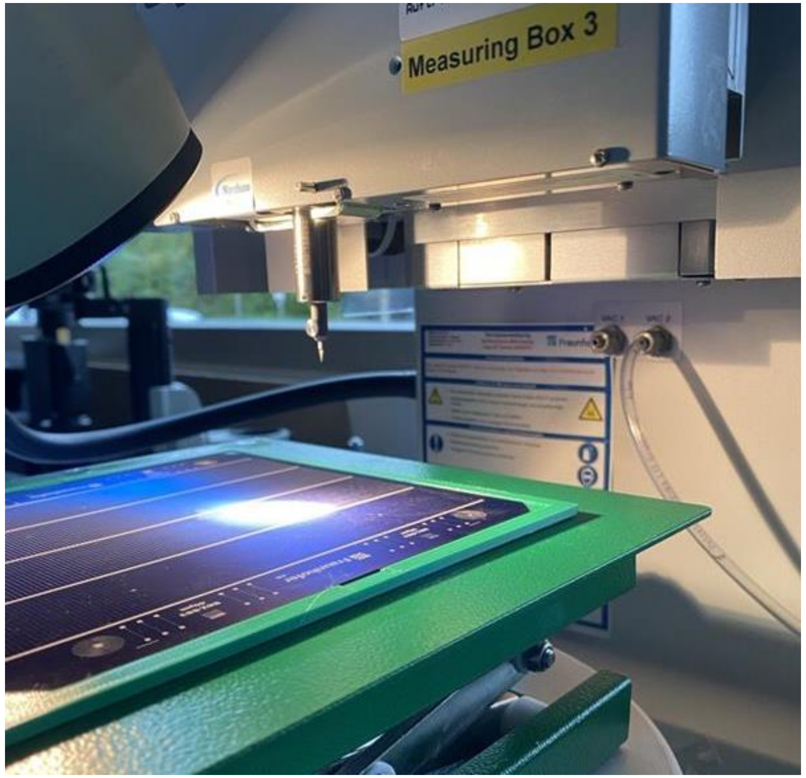
Variation of epoxy resins (ERs)

Adhesion test

- **Stylus test**
- **Shear bond tester**

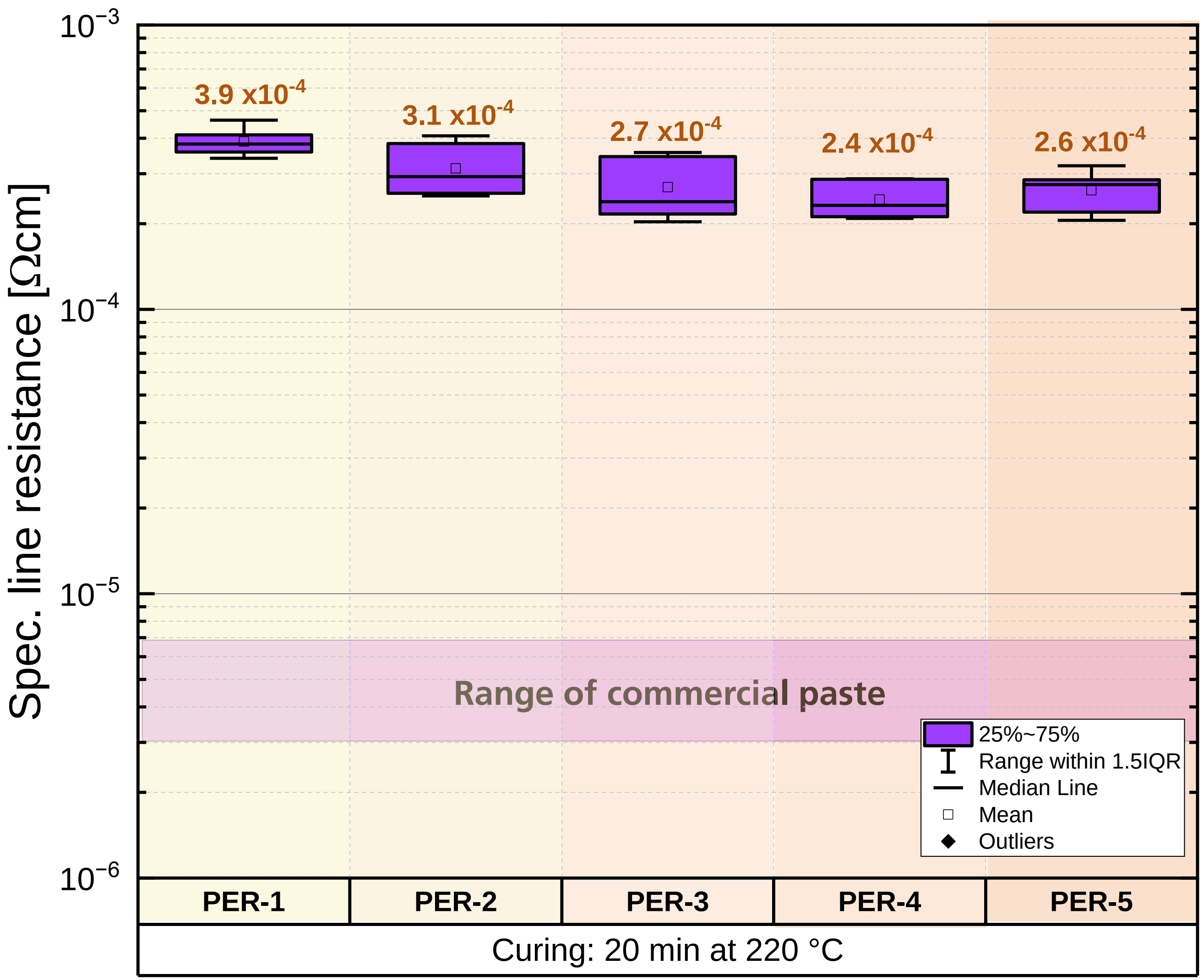


Variation of epoxy resins (ERs)

Specific line resistance

- Close line resistance values
- The higher MW, the better

- ↗ Temperature, ↘ line resistance

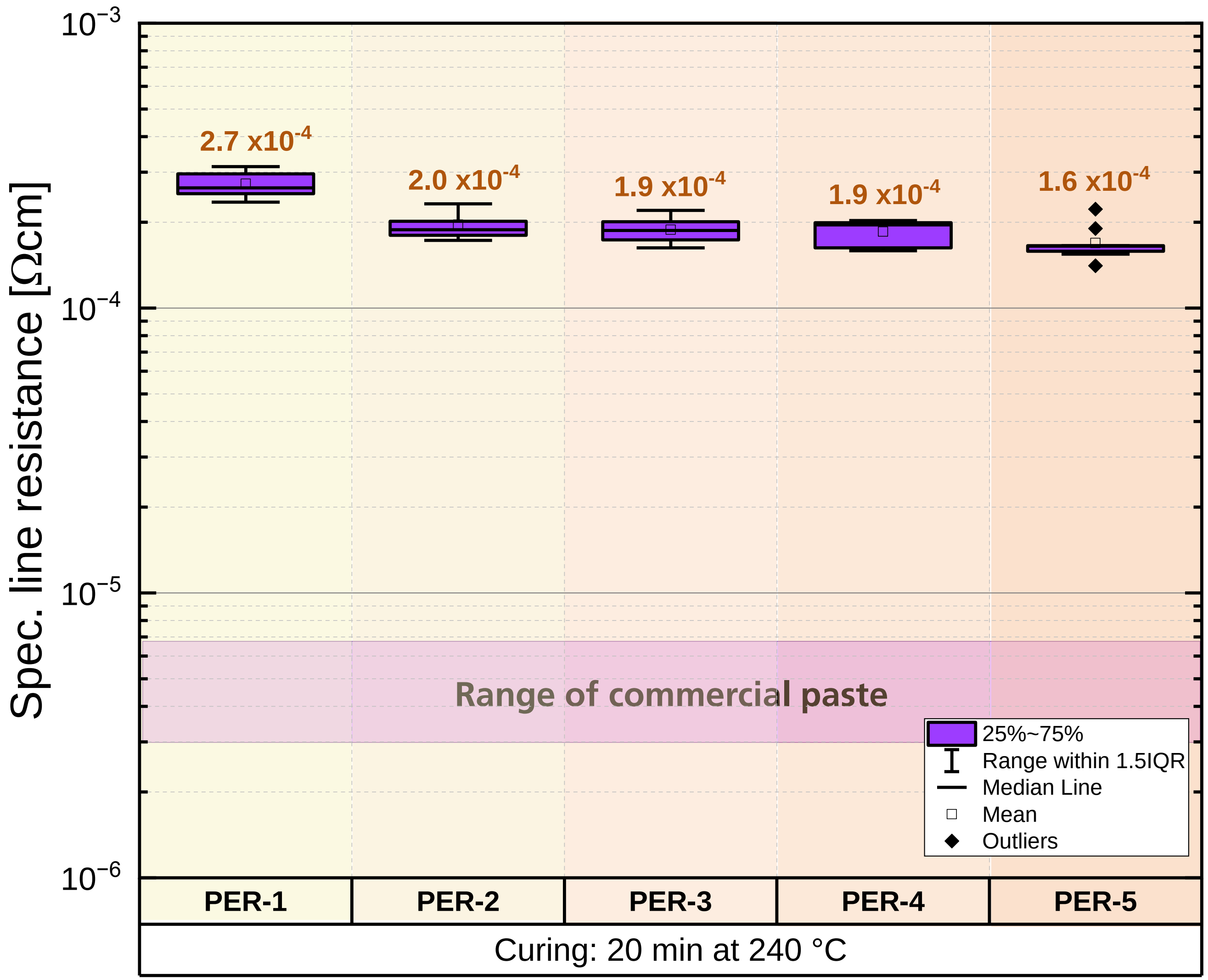


Variation of epoxy resins (ERs)

Specific line resistance

- Close line resistance values
- The higher MW, the lower the line resistance

- ↗Temperature, ↘ line resistance
- Same tendencies
- **PER-5** best conductivity,
- Inverse proportionality to curing



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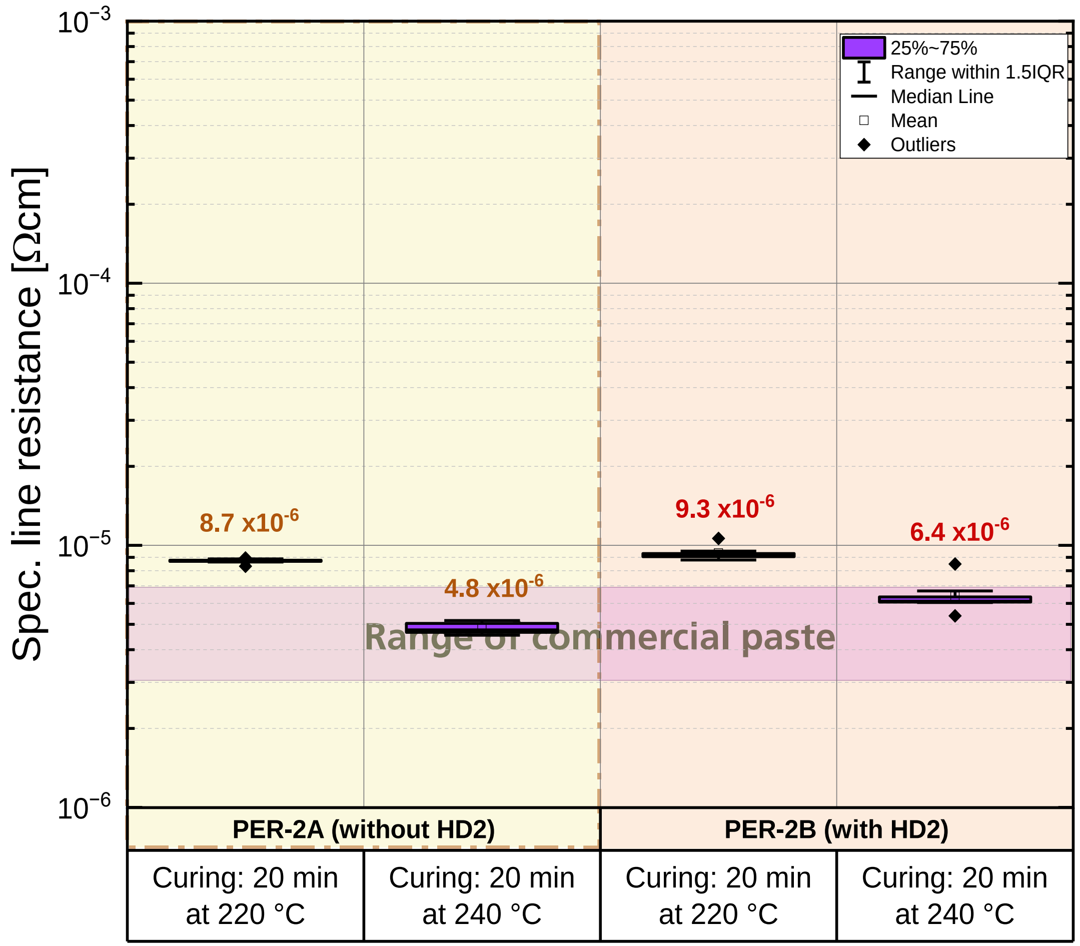
High performing paste

Specific line resistance

- **Requirements:**
- Particles: shape, size , quality
- Higher solid content 95 wt%
- Optimal ratio ER to particles
- **PER-2A:** Enhanced conductivity

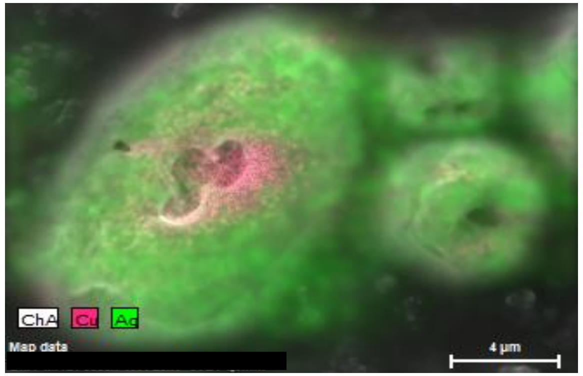


Mhirsi et al., *Progress in Photovoltaics*. (Submitted)
Mhirsi et al., *Manuscript in preparation for Proceedings in IEEE JPV*

Summary

- Traces of copper reach organic phase for pastes with AgCu particles
- Anhydride as alternative to linear primary diamine
- Trade-off between curing and conductivity
- Ratio optimization

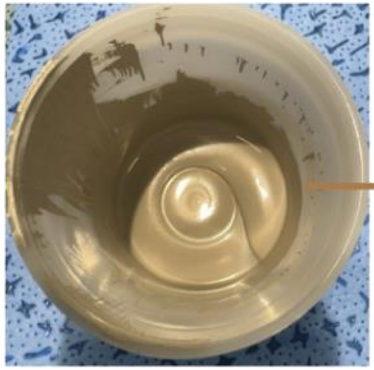
SEM: AgCu

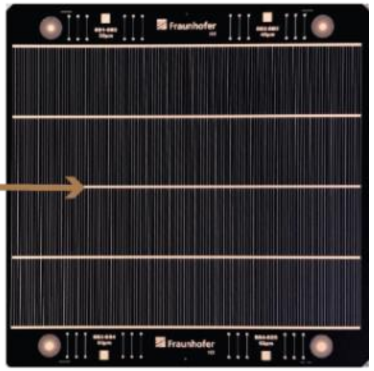


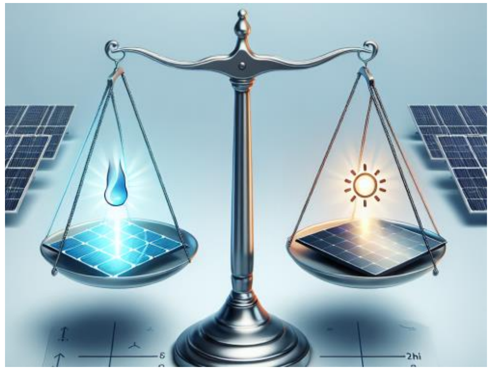
AgCu + ER-2/HD1

AgCu + ER-2/HD2/CAT

AgCu







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Thank you for your Attention!

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