Conductive Pastes and Inks from Base Metal Particles

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Introduction

In the near future, circular economy will increasingly require the use of recyclable, bio-based substrates for printed electronics. Furthermore, for low-price applications the use of base metals with low eco-toxicities is a challenging topic.

In the EU funded project CircEl Paper, ISC evaluates and develops different material concepts for sustainable electronics. In this context, one goal is the replacement of noble metals by low-price, environmentally harmless base-metals as conductors.

Metals

In contrast to noble metals like silver, base metals are covered by an insulating oxide layer, so that electrical conductivity cannot be achieved just by interparticle contacts. A suitable base-metal candidate should have air stability to some extent, and a low melting point is vavourable so that the particles can be welded together at low temperatures, thus breaking up the covering oxide layer. Additionally, measures must be taken to prevent re-oxidation, and of course toxic or environmentally hazardous metals like lead or cadmium must be avoided. Thus, we choose tin and zinc as the most promising candidates. Both metals are commercially available as fine powders of high purity.

Formulation of screen-printing inks

An ink formulation suitable for screen printing should show a thixotropic behaviour, characterized by a sharp decrease of the viscosity with abrupt shear loading, and a recovery of the original viscosity when the shear stress ends.
By optimizing the formulation of the screen-printing pastes, which contained 80vol-% of metal particles and PVP as a polymer binder, the thixotropy time (recovery of 90 % of the original viscosity) could be adjusted to a desirable value of 15-20 s (Figure 1).

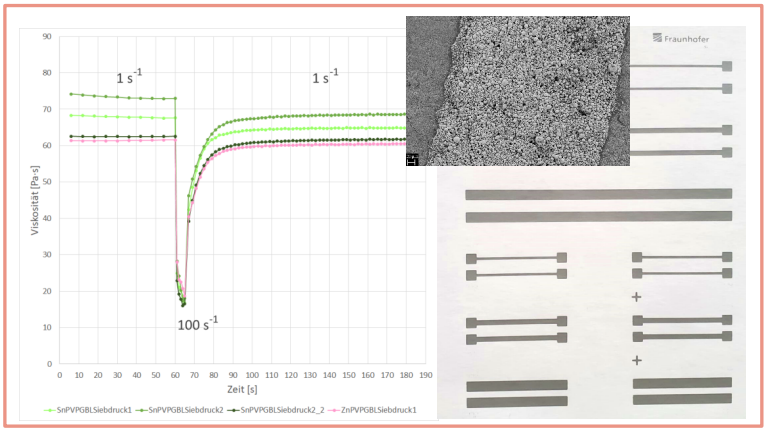
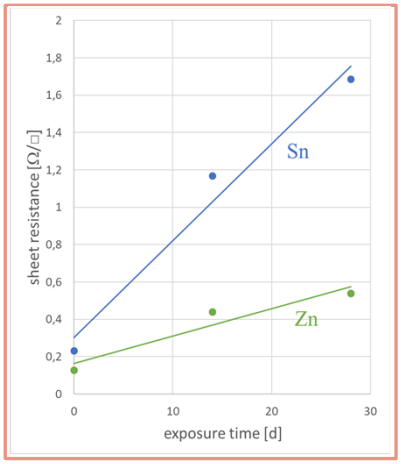


Figure 1: Rheological behaviour of screen-printable inks (left) and screen-printed conductor paths on paper (right)

Printing and Thermal Aftertreatment

After screen-printing of the metal inks, the as-printed pathways did not show measurable electrical conductivity. Thus, a thermal step was necessary to break up the insulating oxide layer on the particles and weld them together, creating conductive paths. After hot pressing, the electrical resistance of printed pathways dropped to values of ~20-500 $\Omega\square^{-1}$ but were only poorly reproducible. Significantly better results were achieved by calendering. The originally dull grey pathways showed a metallic shine afterwards, and their electrical resistance dropped well below 1 $\Omega\square^{-1}$ at a sheet thickness of around 15 µm.

Oxidation Behaviour



After storage in air for several weeks, the electrical resistance of the samples raised slightly due to re-oxidation (Figure 3). In the case of Zn, the formation of needle-like crystals could be observed under the SEM. This could be prevented by addition of an anti-oxidant (Figure 4). If additionally a protective silicone layer is applied, no significant increase in resistance is observed for at least four weeks.

Figure 3: Development of the electrical resistance of printed Sn and Zn conductive paths upon storage in air for several weeks

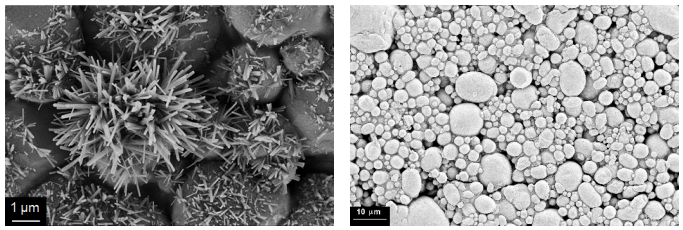


Figure 4: Left: Zn particles without oxidation protection form needle-like crystals of basic zinc carbonate ($2\,ZnCO_3 \cdot 3\,Zn(OH)_2$). Right: The oxidation is prevented by addition of an anti-oxidant

Conclusion

Screen-printing inks were formulated using particles of the base-metals Sn and Zn, respectively. Printed conductive paths showed good electrical conductivities after calendering, and their re-oxidation could be prevented by addition of an anti-oxidant and applying an encapsulation on top.

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