Surface Coatings on High-Voltage Electrodes of Electrostatic Particulate Matter (PM) Sensors

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CoorsTek Sensors

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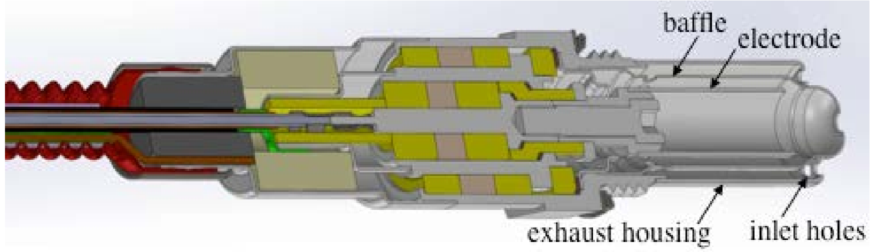
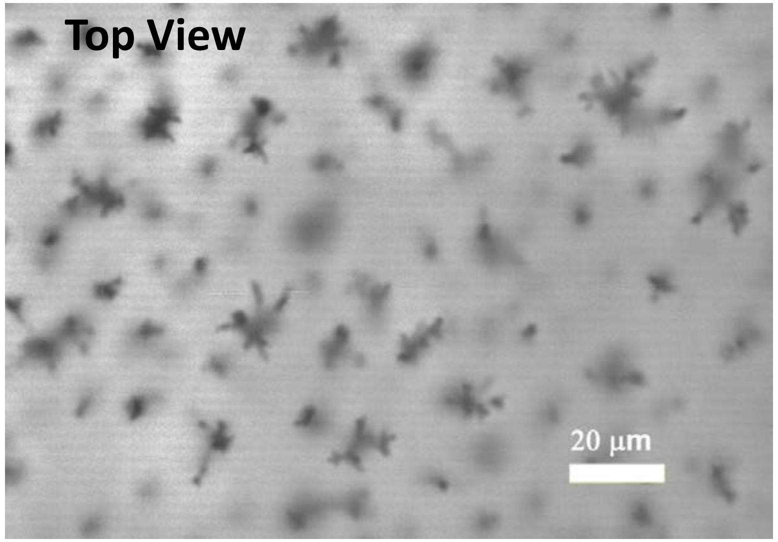
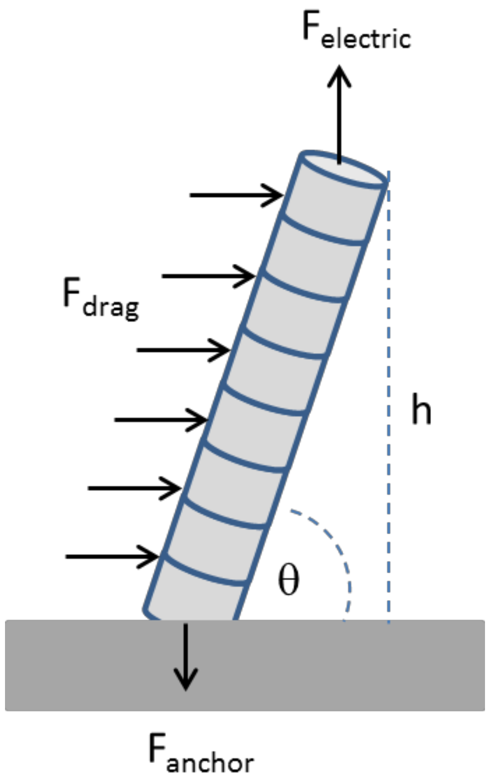
Electrostatic CoorsTek PmTrac sensor for in-situ measurement of soot

- Naturally charged soot; bipolar with ~30% positive and ~30% negative
- Novel measurement with signal amplification, real-time output, simple physical design, and tolerant of contaminants
- Potentially better sensitivity, response times, and durability than resistive-type that rely on burning off accumulation and can have false positives from contamination of repeated cycling
- Apply 1 kV (~800 kV/m field) to concentric electrostatic trap; measured current proportional to PM mass concentration (mg m^{-3})



Measurement principle not completely understood, but seems related to soot growth to critical height





- Captured soot grows filamentous dendrites with high surface charge density that collapse without electric field
- Critical height where electric field exceeds binding force – highly charged fragments deposit on opposite electrode in chain reaction
- Growth, fragmentation, and charge transport – up to three orders of magnitude increase in measured charge current amplification

D. Bilby et al., 2016 PEMS Workshop.

D. Bilby et al., *J. Aerosol Sci.*, **98,** 41 (2016).

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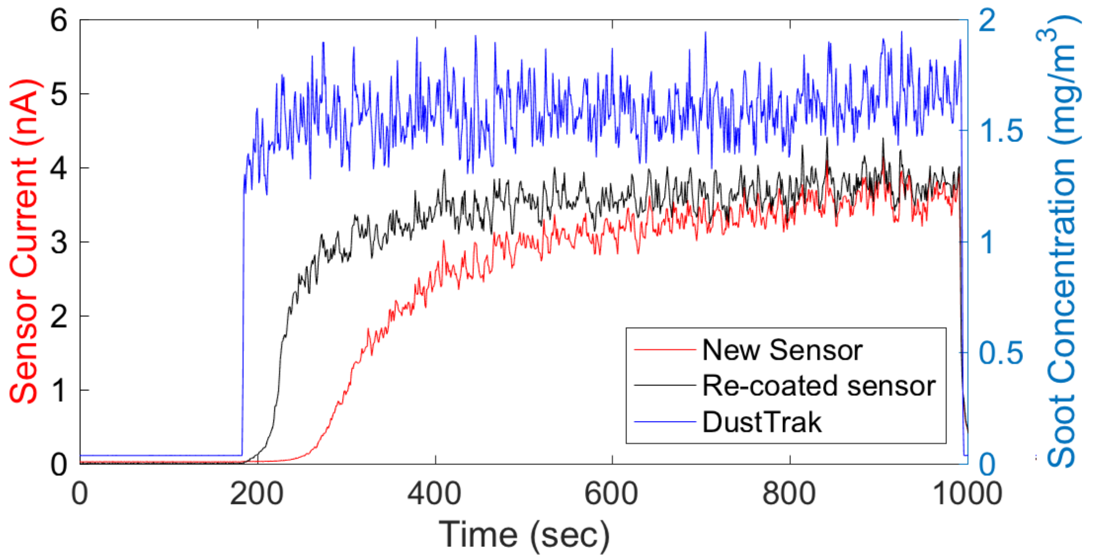
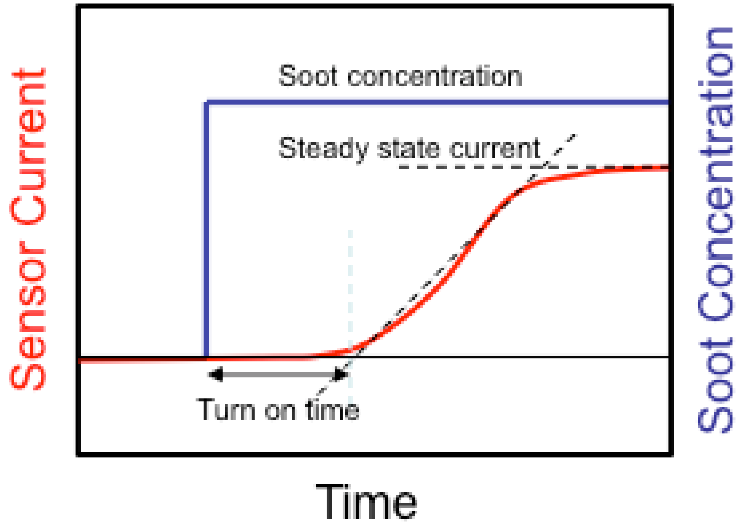
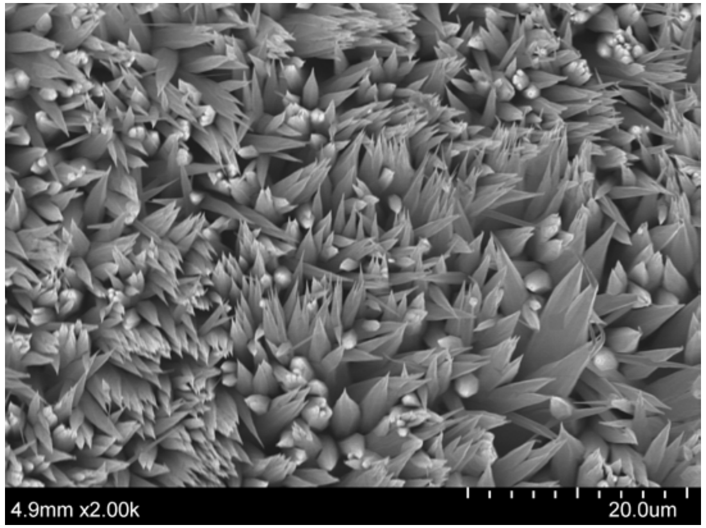
Startup delay in new sensors for reaching steady-state amplification – influence of surface coatings

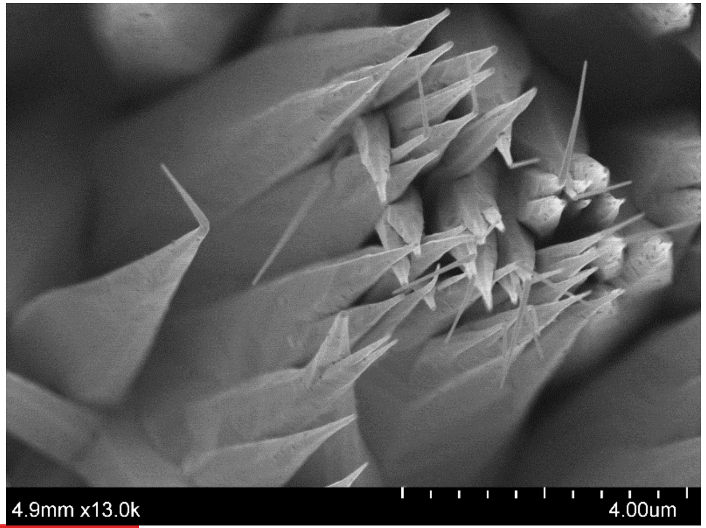
- Reduced delay when operated in higher soot concentrations or when previously operated in soot
- ***Turn on time*** – difference between current rise inflection (extrapolated from rise slope to baseline) and first soot exposure
- Previous work indicated influence of dendritic coatings to reduce turn on time:
  - Rhenium (Re)
  - Nickel-cobalt (Ni-Co)





High temperatures required for dendritic rhenium (Re) – fragile structures made replicating results difficult





- High-temperature chemical vapor deposition (CVD) of dendritic rhenium required refractory metal electrodes (molybdenum)
- Ford measurements indicated that although soot appears on Re peaks, they are much larger than the Re dendrite size
- Repeated measurements did not show robust and reproducible effect – evidence of damage to fragile structures

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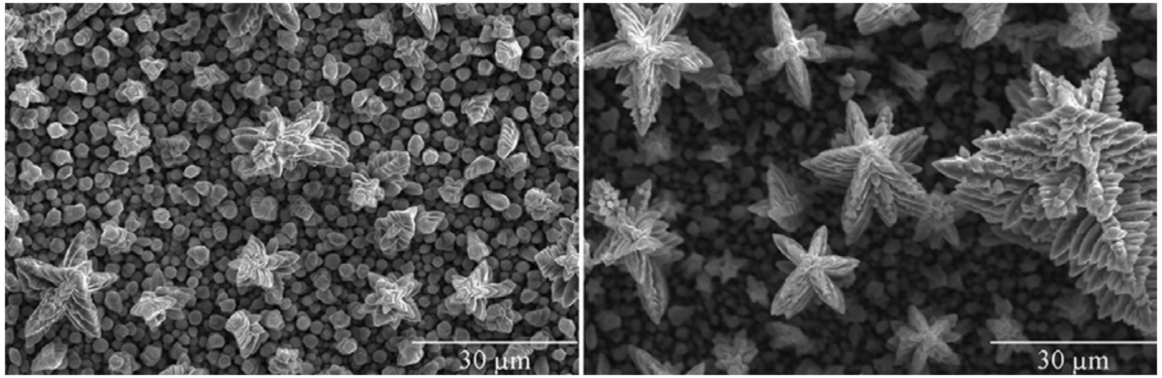
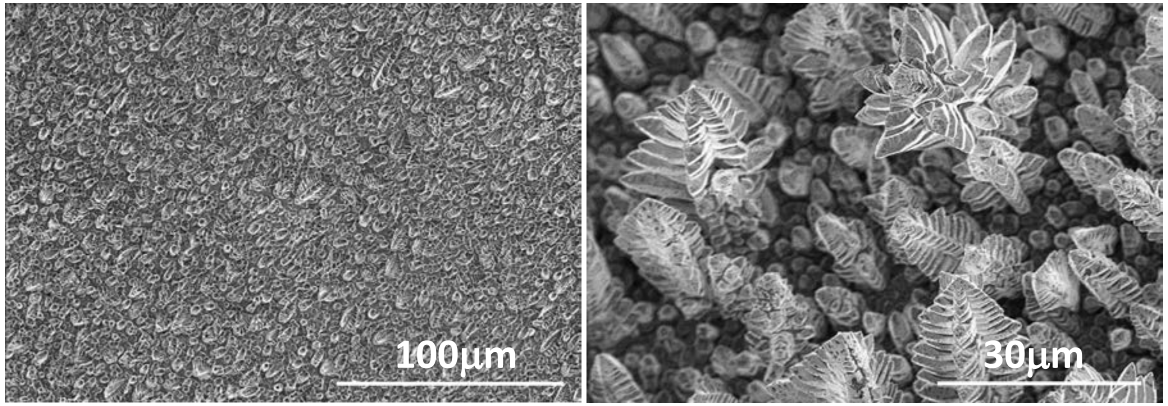
Electrodepositon of dendritic nickel-cobalt (Ni-Co): correlating surface microstructure with turn on time

- Dendritic Ni-Co surfaces using room temperature electrodeposition onto stainless steel cylinders – based on work by Silva et al.
- Altered surface microstructure using current density and number of cycles during electrodeposition



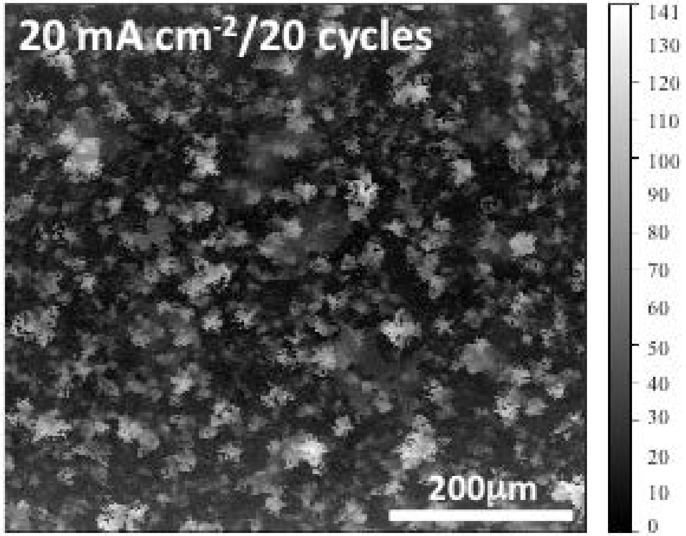
R. Silva et al., *J. Phys. Chem C* , **116**, 22425 (2012).

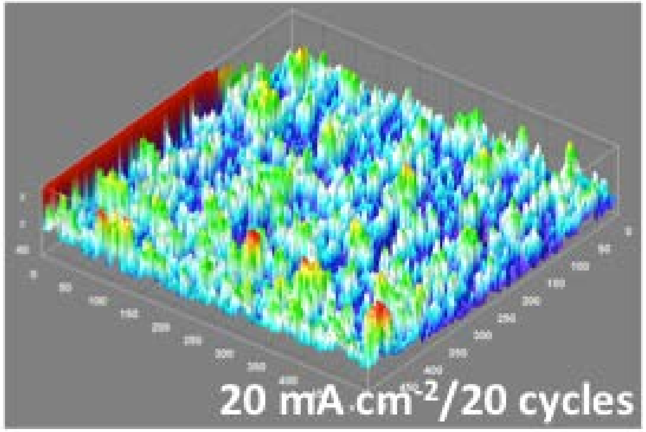


Copenhaver et al., *J. Electrochem. Soc.*, **163,** B234 (2016).

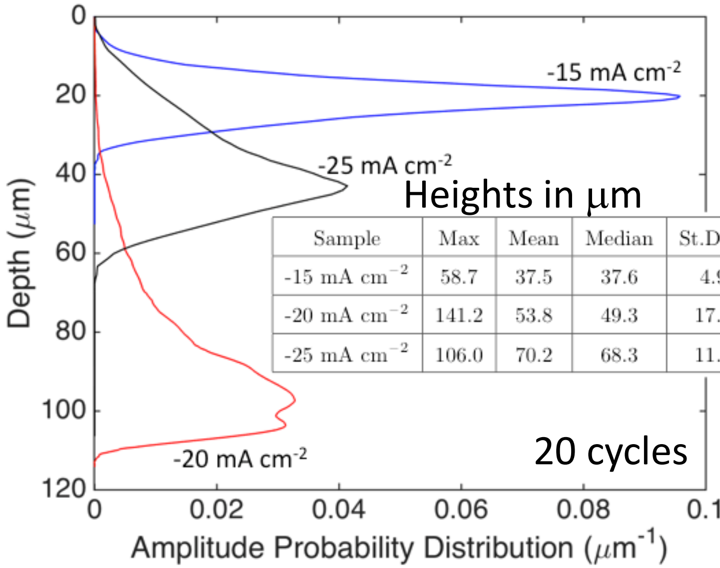
Dendritic coatings – no obvious correlation between surface features and reduction in turn on time

- Laser scanning profilometry and surface height analysis
- Amplitude probability distribution function to quantify relative distributions and heights
- Minor reductions and some increases in turn on time – no clear correlation with surfaces
- Need for model system with good control of properties – Iron (Fe)-based coatings





Three electrodeposition conditions:



Heights in µm

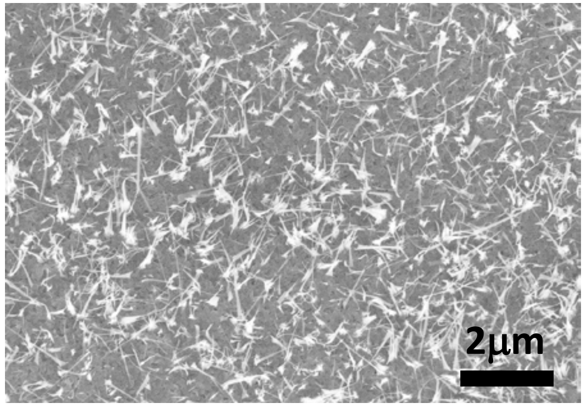
Sample	Max	Mean	Median	St.Dev.
-15 mA cm^{-2}	58.7	37.5	37.6	4.9
-20 mA cm^{-2}	141.2	53.8	49.3	17.1
-25 mA cm^{-2}	106.0	70.2	68.3	11.7

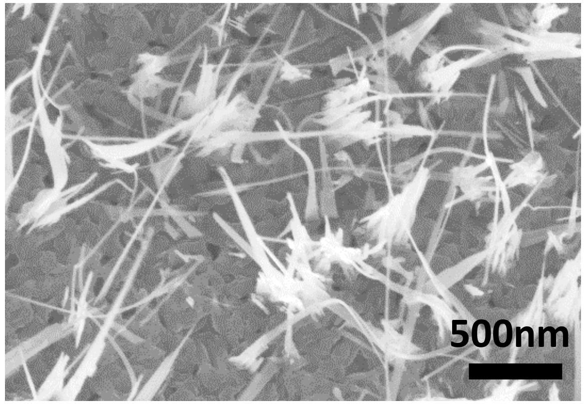
Depth – distance to tallest feature (0 mm); max depth is base of feature

Copenhaver et al., *J. Electrochem. Soc.*, **163,** B234 (2016).

Thermal iron (Fe) oxide coatings

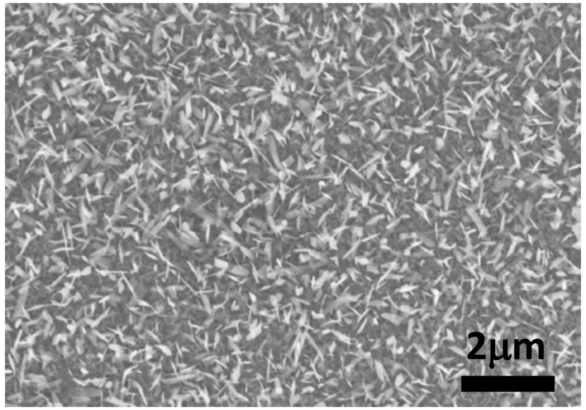
Grown in O_2/Ar

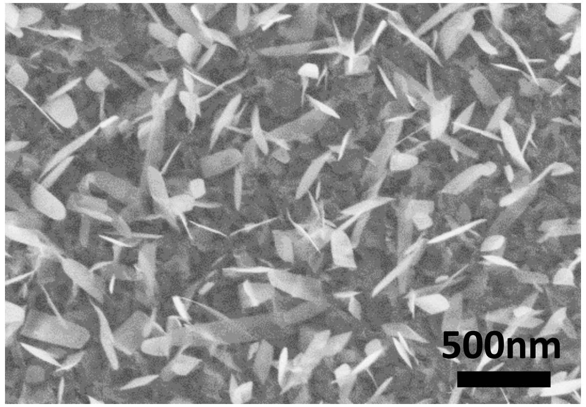




- Heated to 600°C in 2 sccm O_2 and 20 sccm Ar cooling in 20 sccm Ar
- 200 nm – 2 μm thick on Fe
- Fragile but initially robust to ultrasonication

Grown in H_2O/Ar





- Heated to 400°C in 200 sccm Ar bubbled through H_2O cooling in 200 sccm Ar
- 200 nm – 2 μm thick on Fe
- Fragile and not robust to ultrasonication and cleaning

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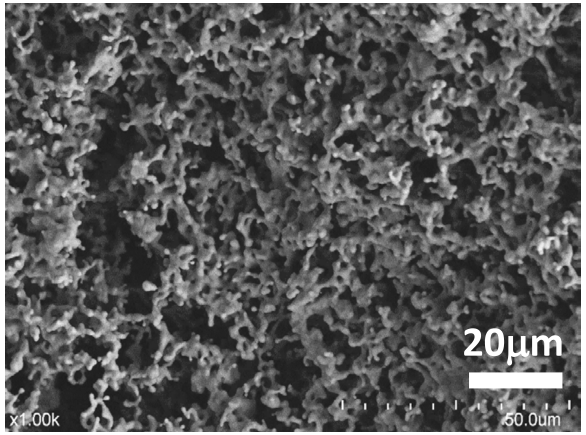
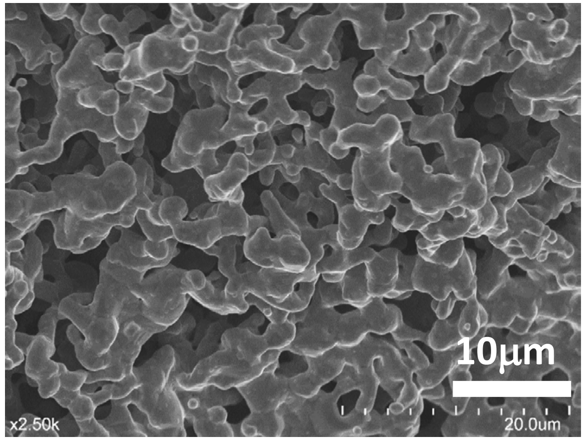
Porous iron (Fe) coatings

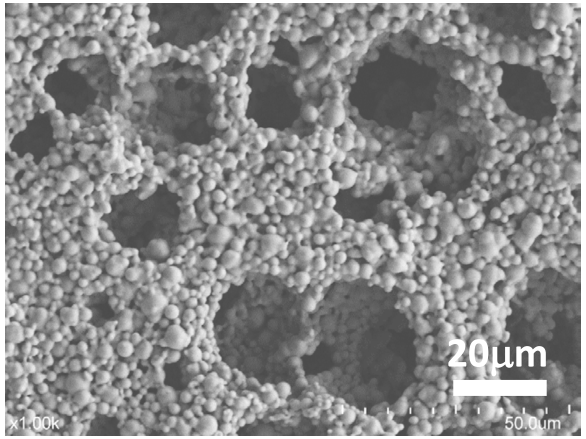
Sol-gel

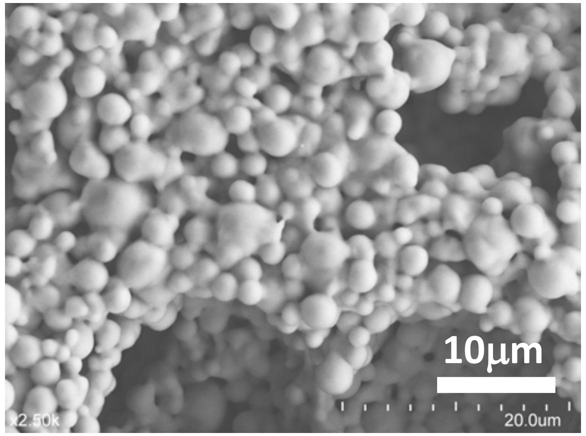




- Nanstructured surface using sol-gel synthesis
- Heated in air to 750°C and cooled in H_2
- 30-50 µm coating on 1 mm Fe
- Robust to ultrasonication and cleaning
- Horizontal shrinkage difficult to control resulted in partial coverage

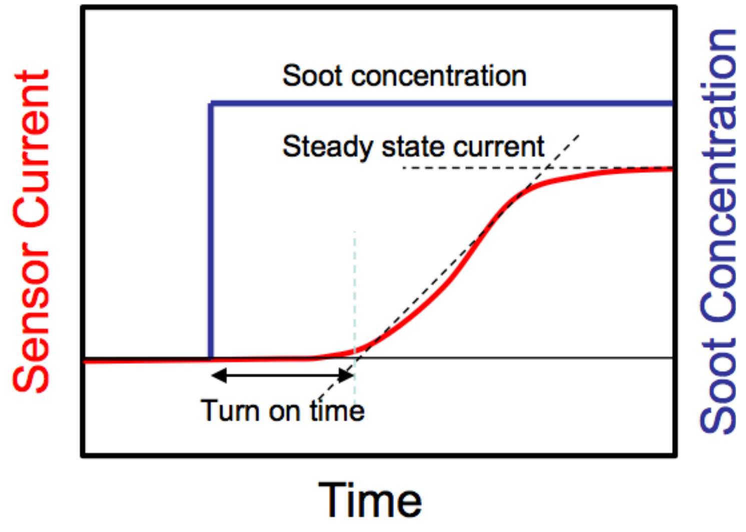
Porous foam



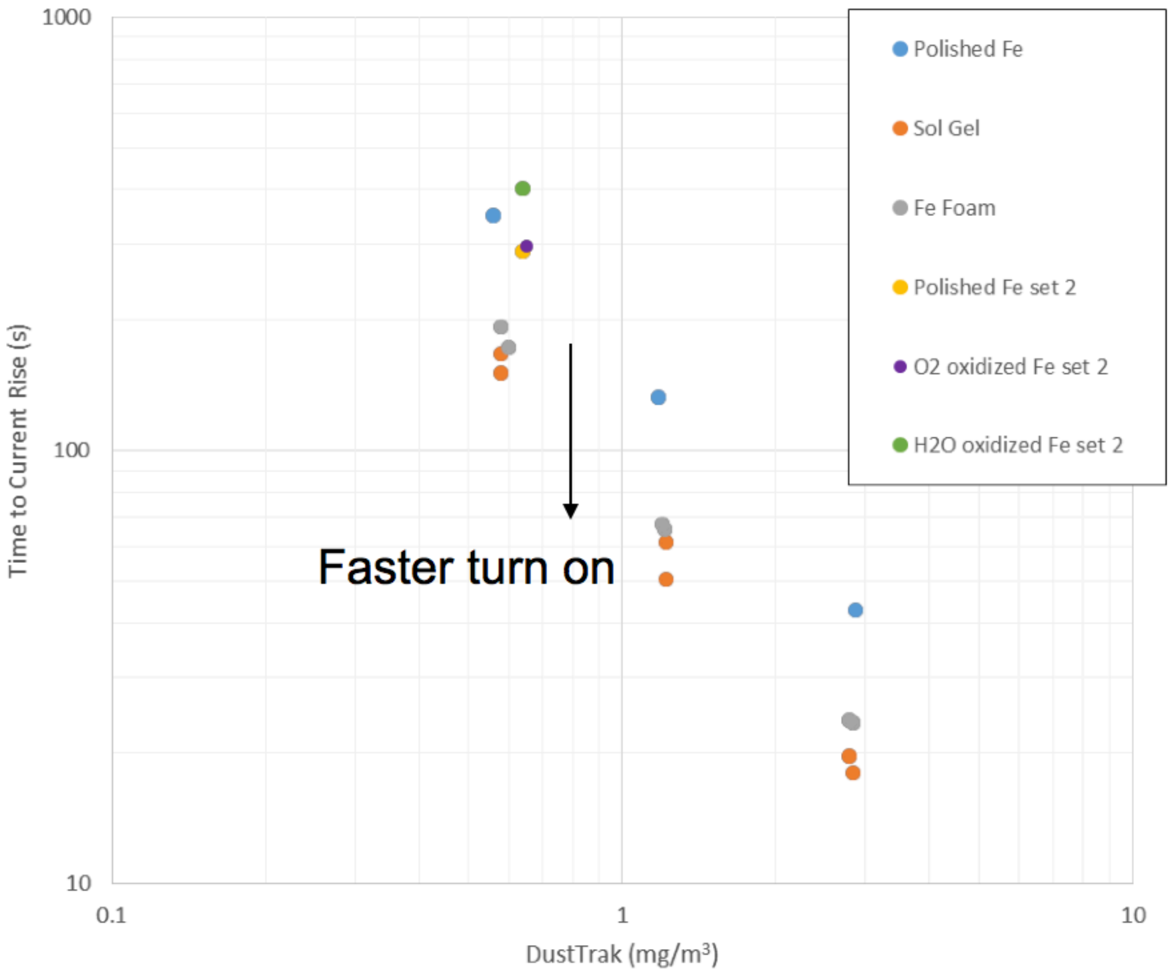


- Fe powder and polymethyl methacrylate (PMMA) beads (spherical voids) solvated in molten polyethylene glycol (PEG)
- PMMA:Fe ratio 50% by volume
- Heated in H_2 to 750°C to prevent oxidation
- 80-100 µm coating on 1 mm Fe
- Robust to ultrasonication and cleaning
- Limited horizontal shrinkage and good coverage
- Other advantages: control of pore size, porosity and thickness

Evaluated at Ford in parallel plate setup and CAST2 soot (avg d_m~80 nm) – tested in similar pairs

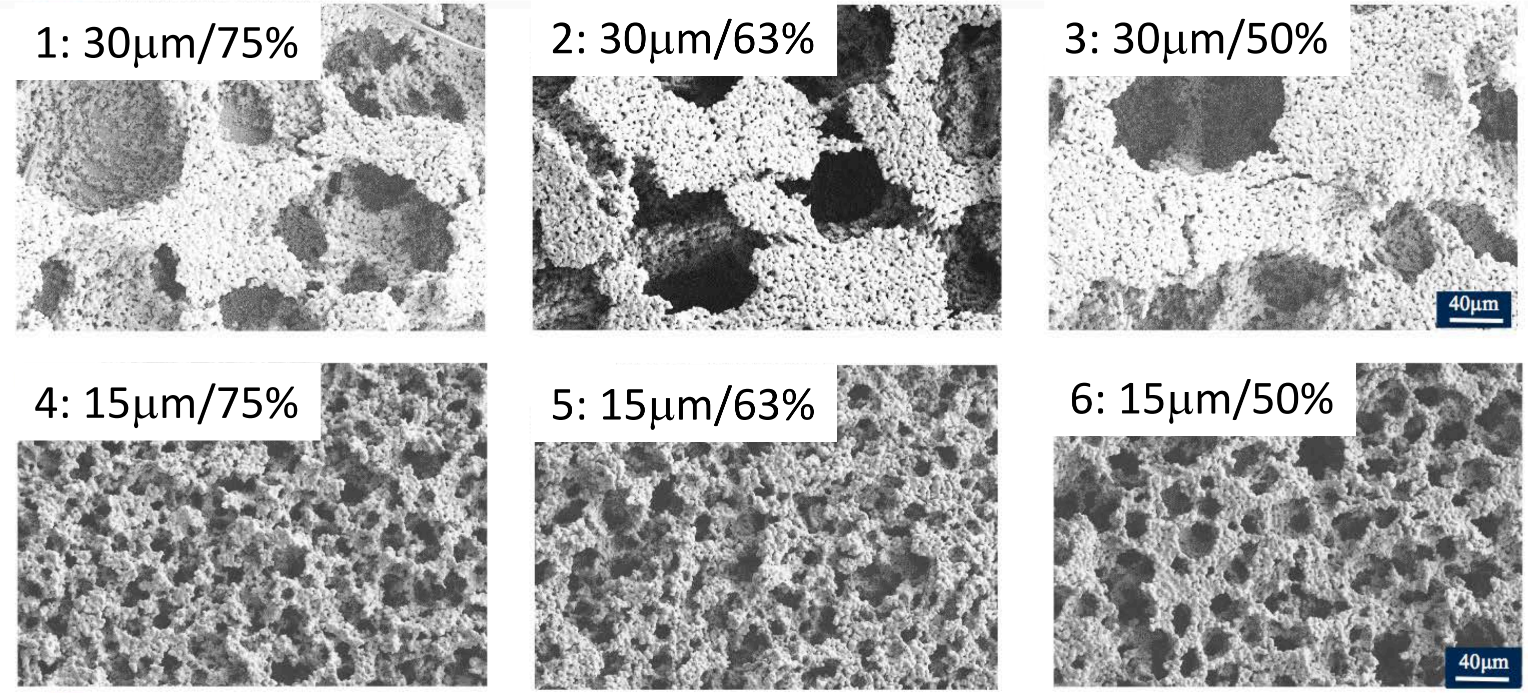


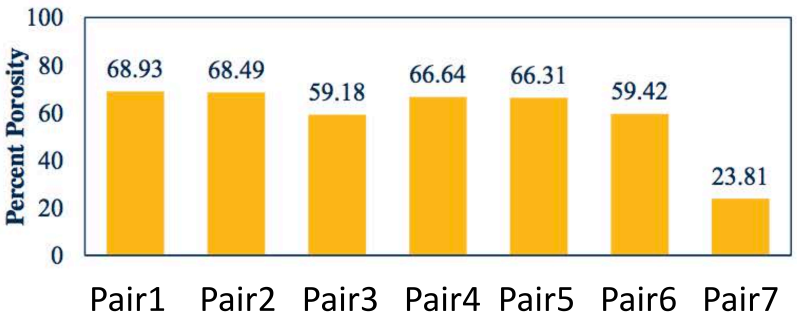
Turn on time: difference between current rise inflection (extrapolated from rise slope to baseline) and first soot exposure

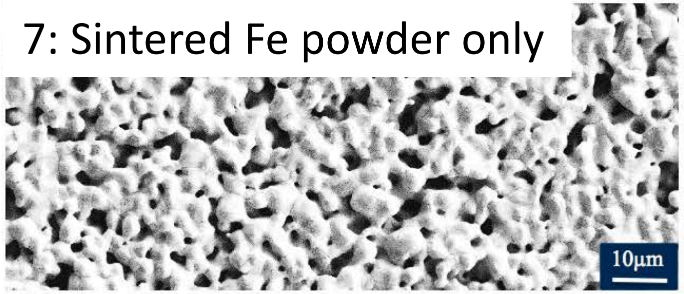


- Tested multiple times after cleaning – ethanol sonication and blown dry
- Thermal Fe oxide too fragile for cleaning and only tested once
- Porous Fe showed faster turn on than polished Fe

Robust reproducible behavior of Fe foam – modify surfaces with different size and volume of pore formers

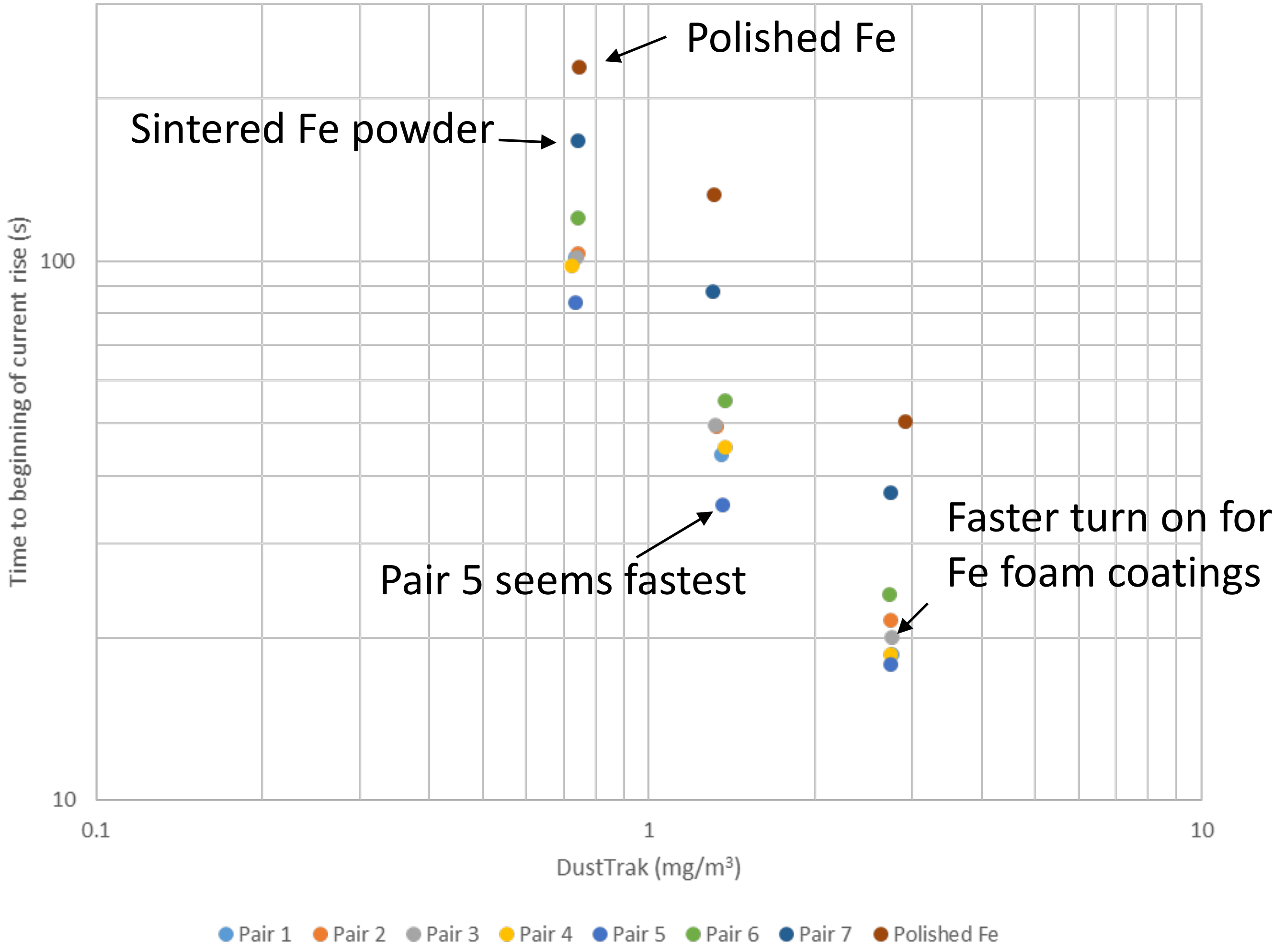


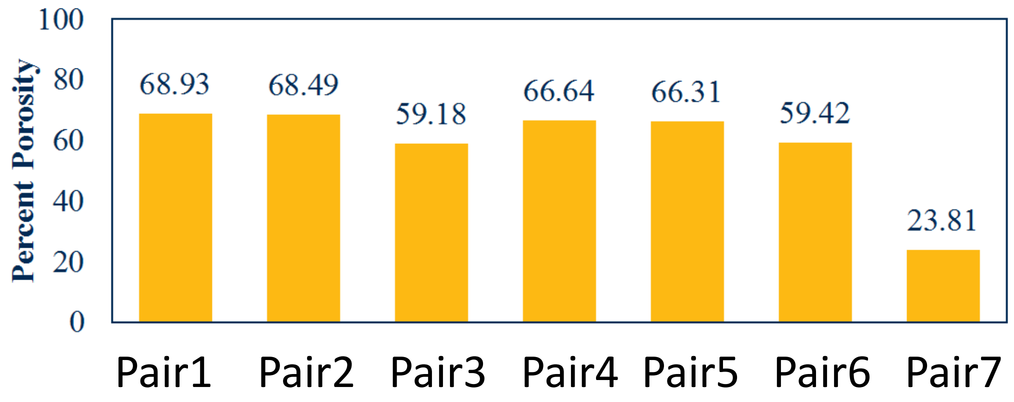




- Fe powder with 1-5 μm particle size
- PMMA pore former with average size of either coarse 30 μm or fine 15μm resulted in different pore size distributions
- Minimal variation in surface porosity likely due to coating thickness of 100-200 μm dominating structure development

Iron (Fe) foam coatings – greater reduction in turn on time from polished Fe compared to sintered Fe





- Sintered Fe powder did show reduction in turn on time compared to polished Fe
- Fe foams consistently showed larger reductions in turn on time compared to Fe powder and polished Fe
- Indications that an increase in porosity from sintered Fe to porous Fe resulted in further reduced turn on time

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Summary and Conclusions

- Previous work indicated dendritic coatings on the high voltage electrodes of electrostatic PM sensors could reduce turn on time (i.e., delay in reaching steady-state amplification)
- Larger reduction in turn on time for porous iron (Fe) coatings compared to sintered Fe coatings with lower porosity indicate potential role of surface morphology
- Indicates possible role of surface morphology to reduce the turn on time by reducing the amount of soot interaction needed to reach fragmentation and amplification
- Ongoing work to look at patterned/templated structures with defined geometries

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Questions? Thank you for you attention! lw@emisense.com