Processability of Nanographite-Nanocellulose based electrodes for flexible energy storage applications

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TAPPI

Towards flexible energy storage

New materials

Processing techniques

Environmentally friendly

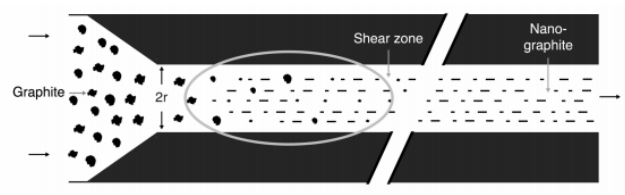
https://tinyurl.com/y63zg5dk
https://tinyurl.com/y626d2z2
https://tinyurl.com/y34jlzd3

https://tinyurl.com/y2vp8zq3
https://tinyurl.com/yxzkewdg
https://tinyurl.com/y5bmjvst

Objectives

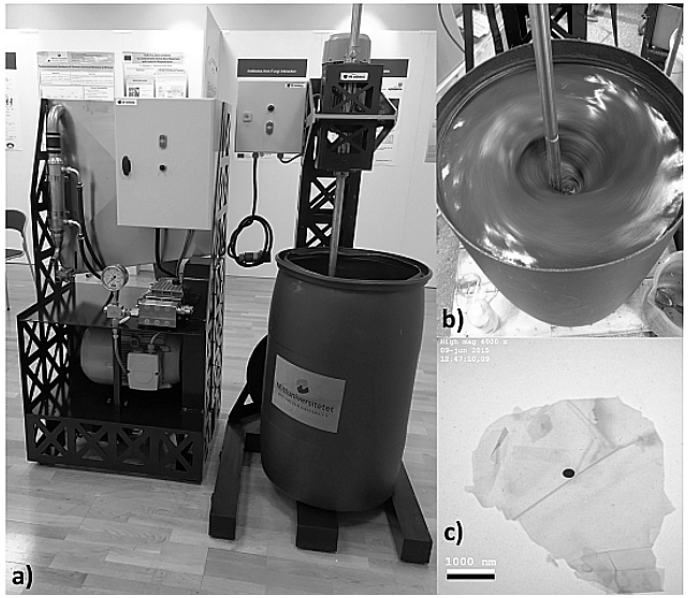
- Continuous roll-to-roll coating of Nanographite-Nanocellulose suspensions onto flexible substrates to produce conductive electrodes
- Understand various factors that influence the coatability of the suspensions and their corresponding electrical properties
- Demonstrate an energy storage device (supercapacitor) fabricated from the said electrodes

Nanographite production



Schematic of tube-shear exfoliation

- Thermally expanded graphite (EXG 9840, Graphit Kropfmühl, Germany) as starting material
- 2 wt.% aqueous suspension
- Large amount of multi-layer graphene and graphite nanoplatelets
- High specific surface area – beneficial for electrodes



(a) Hydrodynamic tube shearing device; (b) dispersion barrel during stirring (to avoid graphite flotation); (c) TEM-image of Nanographite

Blomquist N. et al., PLoS ONE (2016)

Nanographite-Nanocellulose suspension

- Nanocellulose (TEMPO-CNF) added as a binder to Nanographite suspension
- Nanographite and Nanocellulose ratio – 90:10
- Final suspension solids – 3.5 wt.%

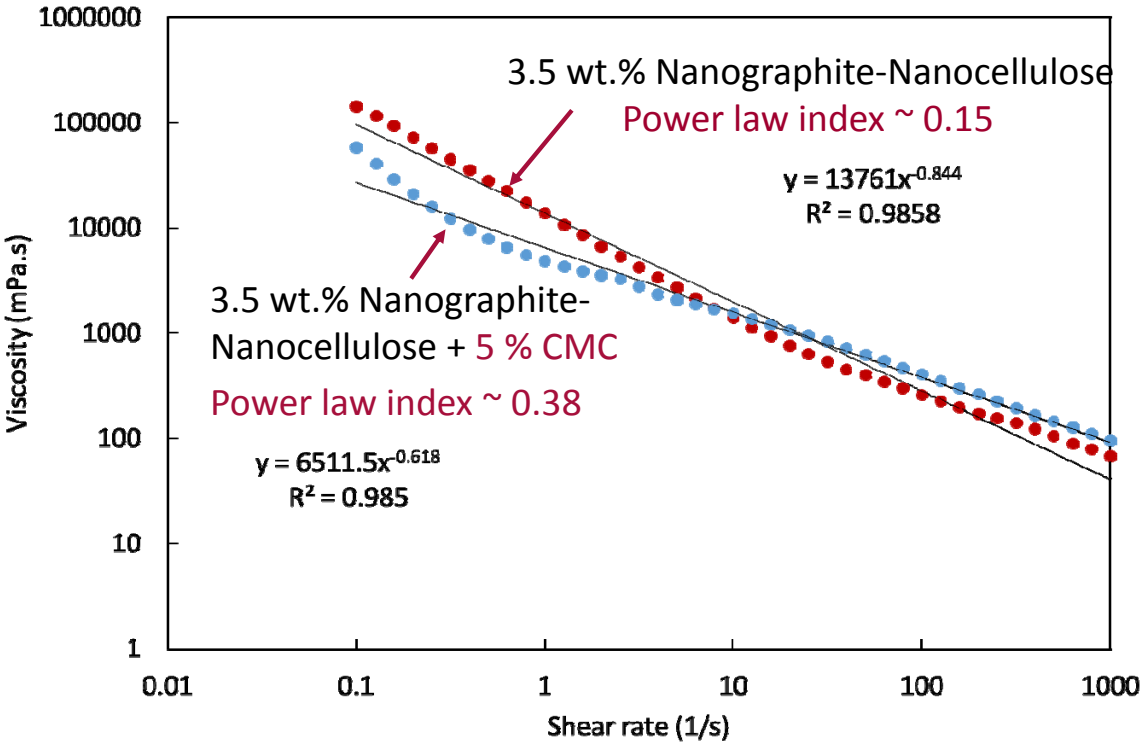
Challenges during processing:

- High viscosity and yield stress
- Low solids content
- Low water retention

No CNF 10% CNF

Andres B. et al., Phys. Status Solidi B (2014)

Rheology of Nanographite-Nanocellulose suspension

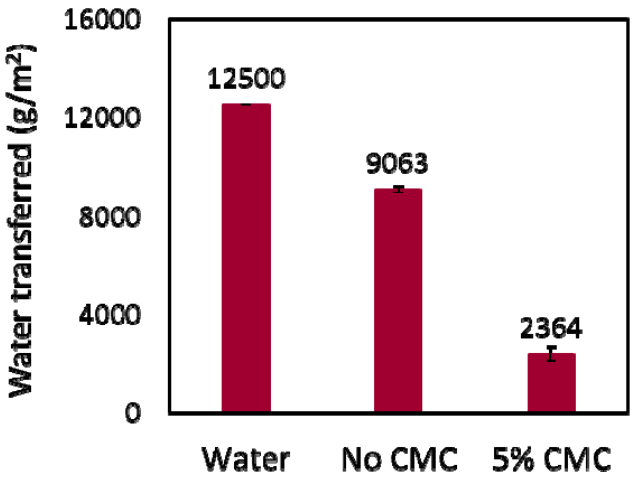


Measured using Anton Paar MCR300 – Couette geometry

- 5 % CMC* (on total dry weight) added as rheology modifier
- Highly shear thinning!
- This behavior can be leveraged by passing the suspension through a narrow slot

*CMC – Carboxy methyl cellulose, Finnfix 4000G (CP Kelco)

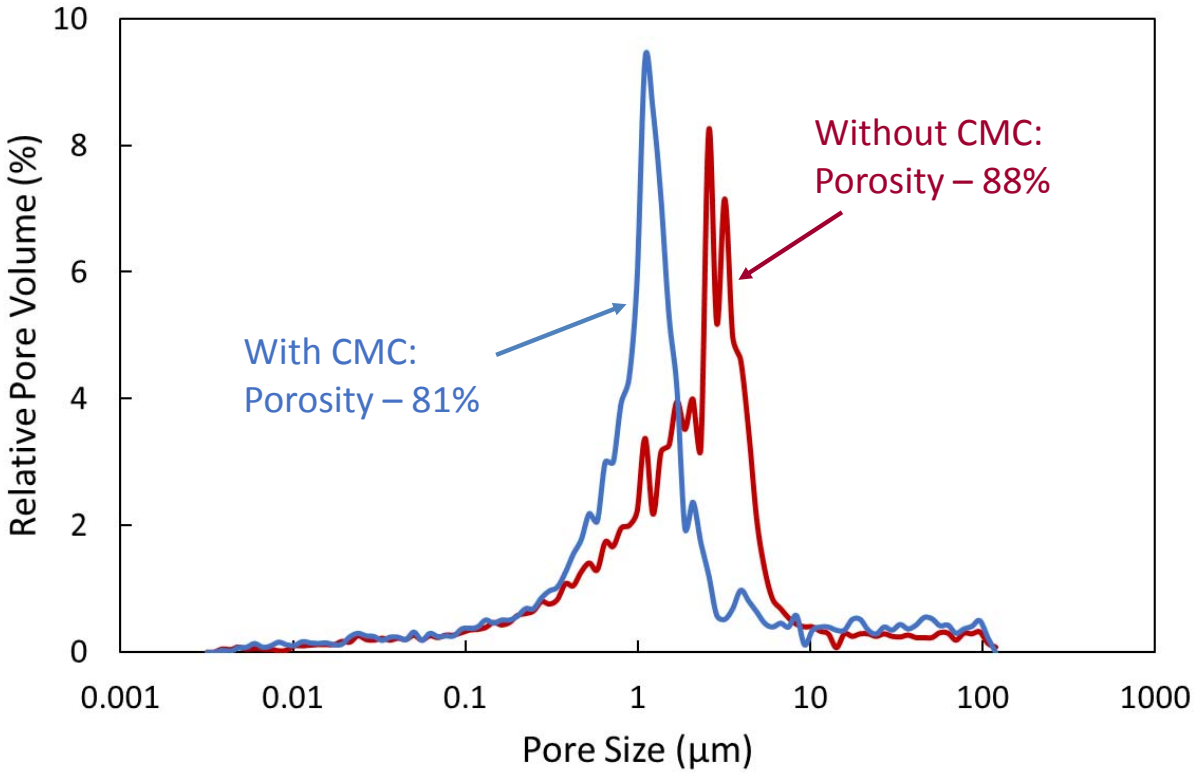
Gravimetric water retention



Measured using Åbo Akademi Gravimetric Water Retention device (ÅA-GWR)

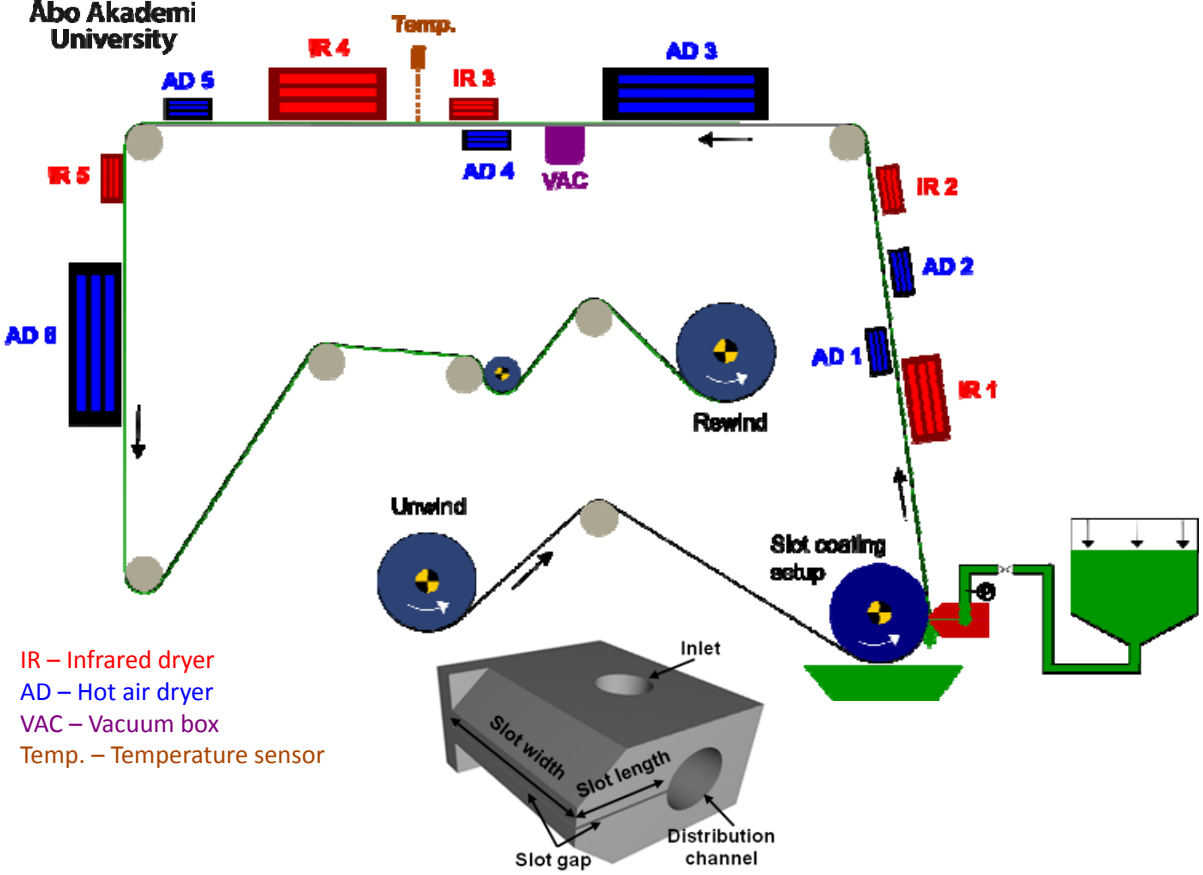
- Pressure filtration: Filter membrane – 5 µm; ΔP – 0.5 bar; Time – 90 s
- Simulates dewatering rate during coating process (water loss from coating to substrate)
- Very low water retention (higher water transfer)!
- CMC addition reduces water transfer by 75%
- Higher water retention (lower water transfer) → better runnability and uniform coating

Porosity and pore size distribution



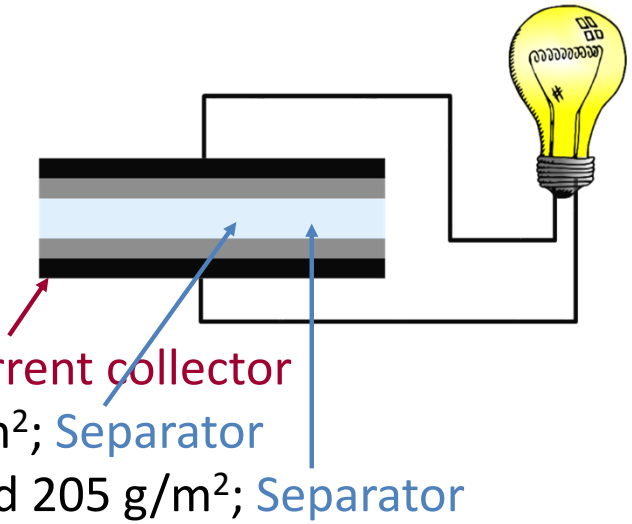
- Mercury intrusion porosimetry of pressure filtered and air dried cakes
- Without CMC → Higher porosity, larger pores and wide size distribution → better electrode performance
- With CMC → Lower porosity, smaller or blocked pores and lower conductive surface area→ poor electrode performance

Roll-to-roll coating process



- Mini-pilot scale custom built setup based on RK Koater
- IR & hot air drying
- 150 mm web, 1-50m/min speed
- Custom fitting of slot die (length: 34 mm, width: 74 mm, slot gap: 50 – 1000 µm)
- Adjustable gap between substrate and slot-lip for coat weight control

Coating parameters



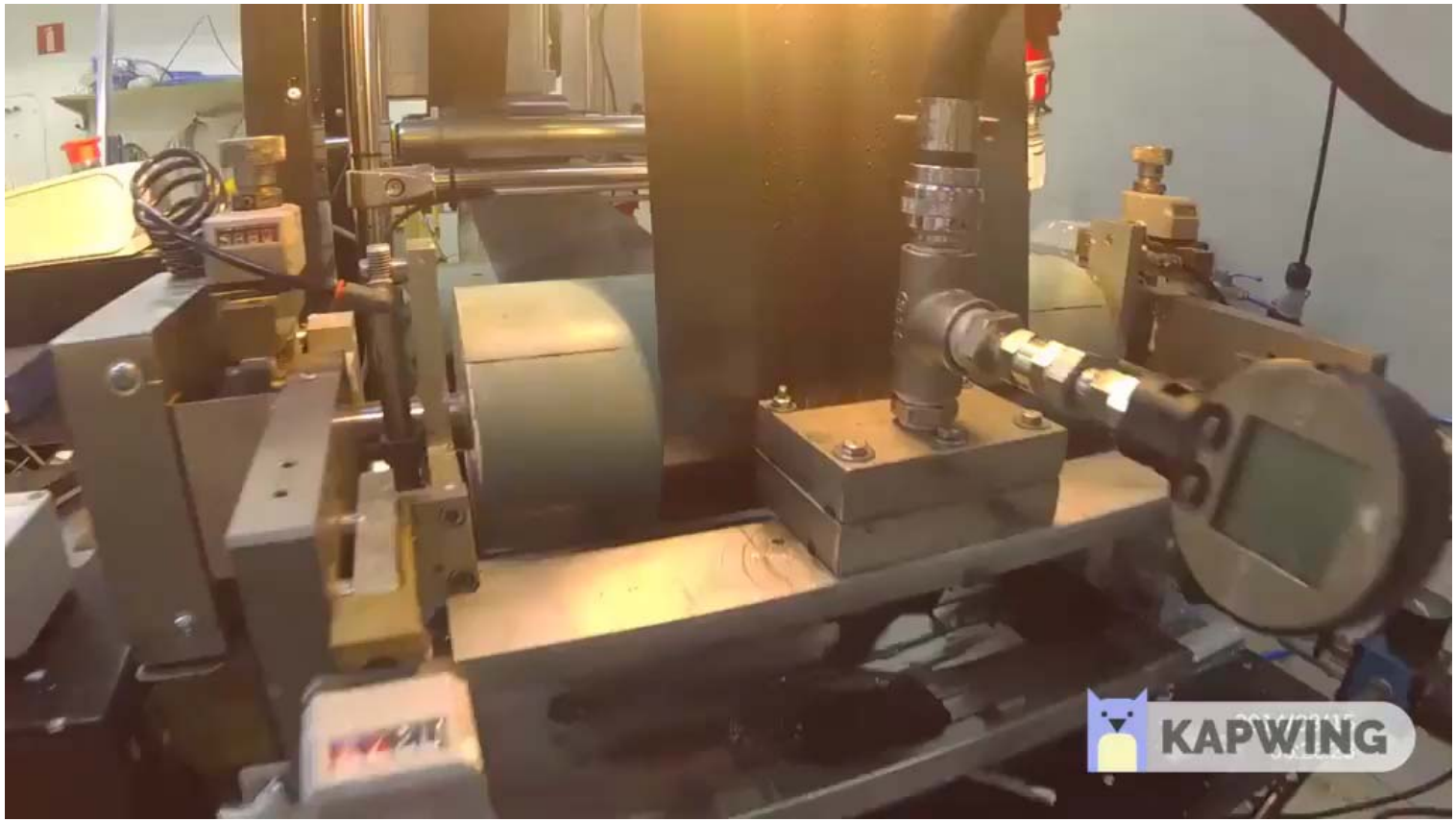
- Substrates:
  - **GF**: Graphite foil (SGL Group); 200 µm and 245 g/m^2; Current collector
  - **KP**: Greaseproof paper (Nordic Paper); 50 µm and 45 g/m^2; Separator
  - **PB**: Pigment-coated paperboard (Stora Enso); 270 µm and 205 g/m^2; Separator

- Suspension:
  - 3.5 wt.% Nanographite-Nanocellulose suspension on GF,KP and PB
  - 3.5 wt.% Nanographite-Nanocellulose + 5% CMC on PB

- Wet coating thickness: 300 µm and 2x300 µm (double coated)

- Line speed: 3 m/min

Coating process



Effect of CMC

No CMC

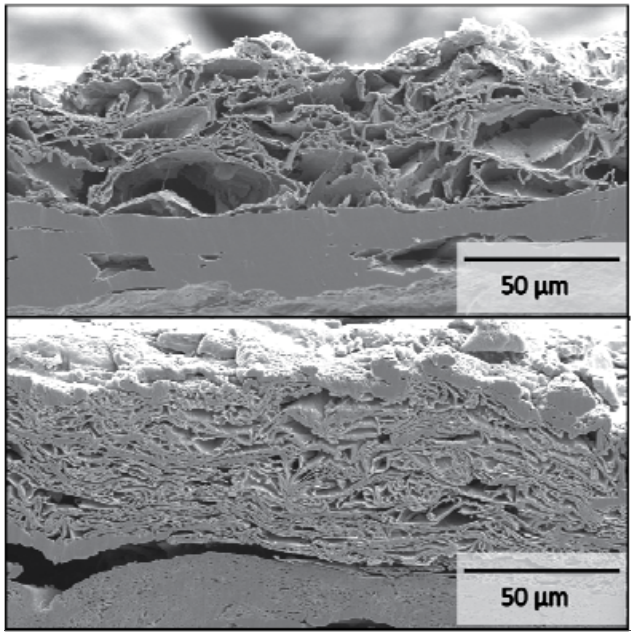
5% CMC

CMC addition → better runnability and uniform coating

SEM cross-sections - GF

GF300

GF600

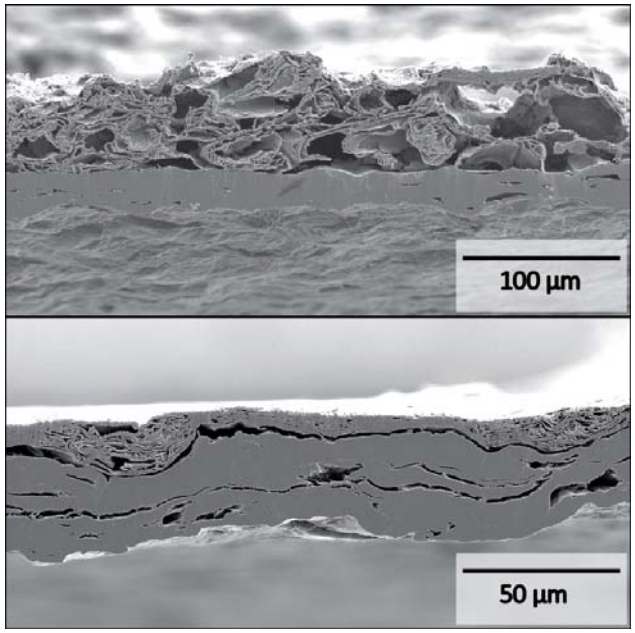


- Two wet coating thicknesses – 300 µm (GF300) and 2x300 µm (GF600)
- Porous electrode layer → better accessibility for ions
- Calendering fuses the electrode and foil together!

SEM cross-sections - KP

KP300

KP300 Calendered

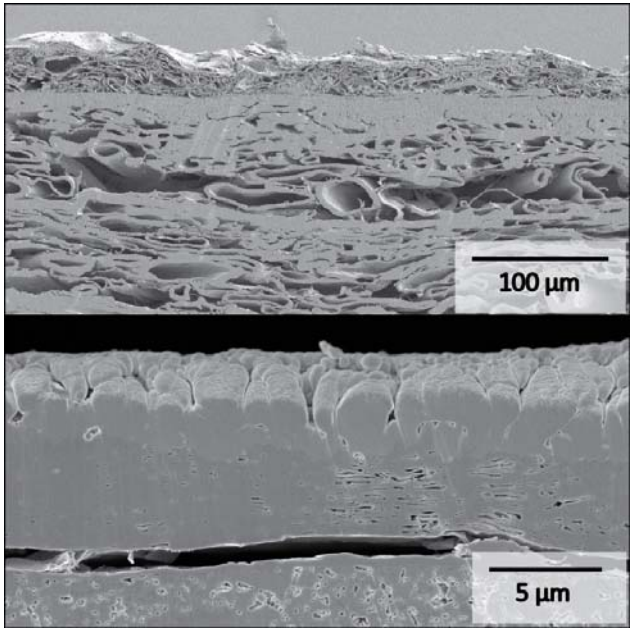


- Two wet coating thicknesses – 300 µm (KP300) and 2x300 µm (KP600)
- Calendered at 60 °C and 100 kN/m line load
- Over 85% electrode compression due to calendering! → lowers electrical resistance but poor access to ions
- Substrate roughness leads to porosity variations in X/Y-plane after calendering

SEM cross-sections - PB

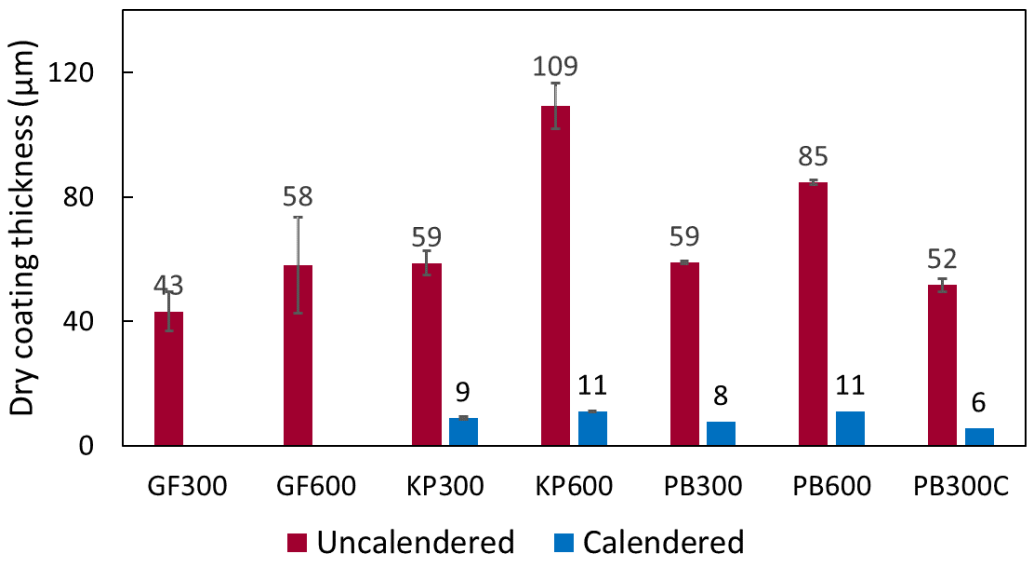
PB300

PB300
Calendered



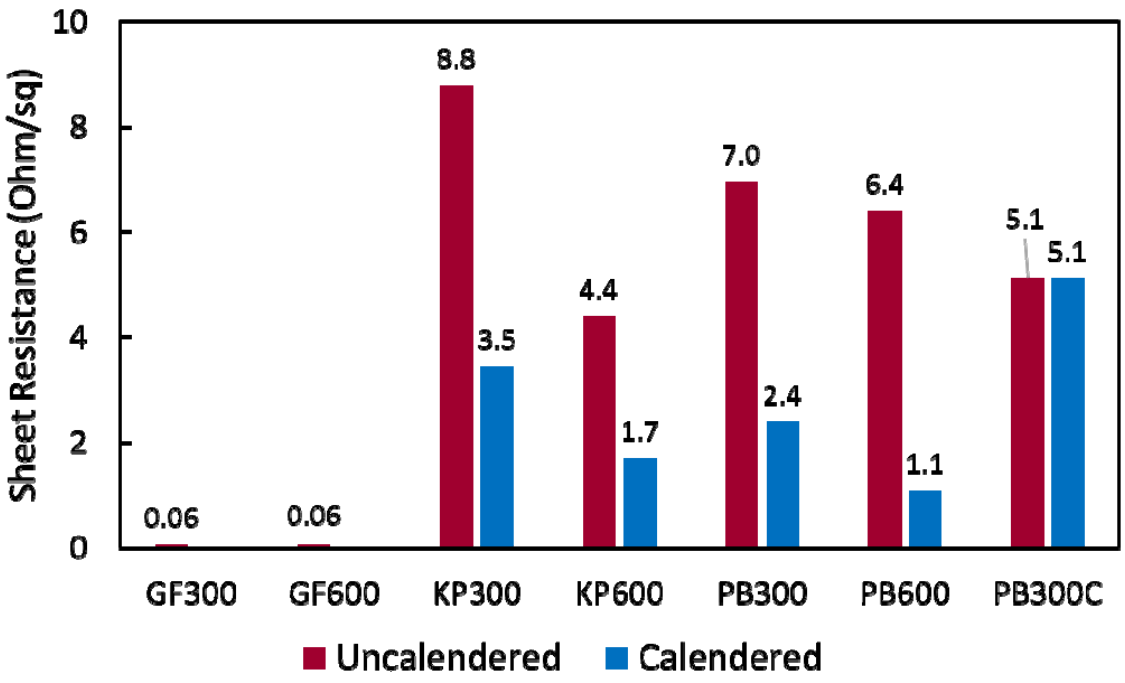
- Two wet coating thicknesses – 300 µm (PB300) and 2x300 µm (PB600)
- 300 µm wet coating with CMC (PB300C)
- Calendered at 60 °C and 100 kN/m line load
- Calendering → dense electrode (~65% compression)
- Smoother substrate → uniform electrode after calendering

Coating thicknesses



- Over 85% reduction in thickness after calendering
- Paperboard has lowest variation → smooth surface and two sided drying

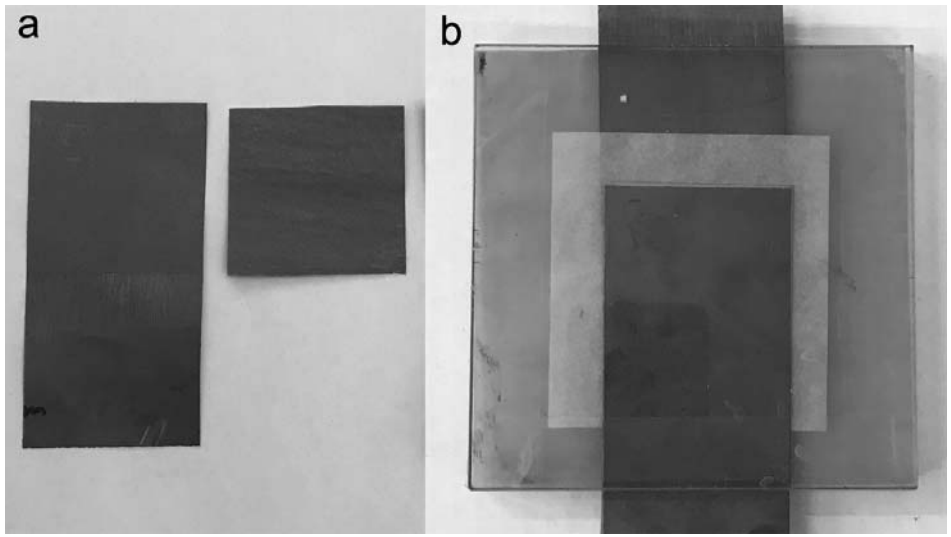
Sheet resistances



Measured using Keithley four-point-probe system

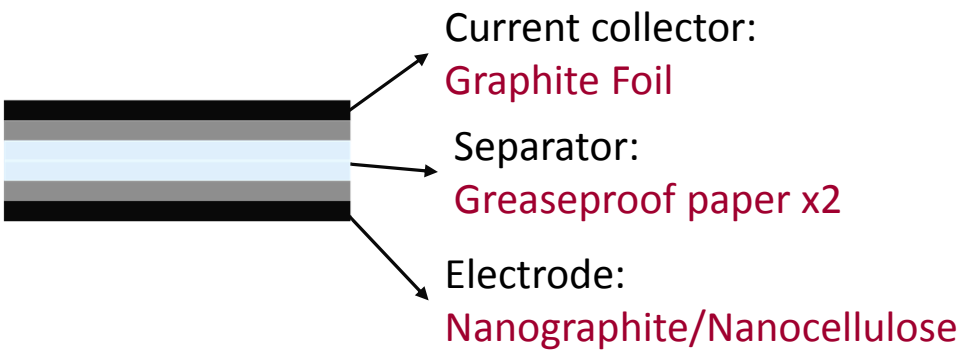
- Graphite foil has the lowest sheet resistance → electrode on conductive substrate
- Calendering → 60 – 80% reduction in sheet resistance
- Calendering has no effect on electrodes with CMC

Supercapacitor assembly



(a) Electrode coated GF (left), KP (right)
(b) Assembled supercapacitor device

- Two configurations. Electrode coated on:
  - Graphite foil (GF) - uncalendered
  - Greaseproof paper (KP) – uncalendered



- Electrolyte: Aqueous H_2SO_4 (1M)
- Cell size: 50 mm x 50 mm

Supercapacitor performance

Electrode coated on:	R_s* (Ω/sq)	ESR† (Ω)	Specific capacitance (F/g)
GF300	0.06	0.88	70.0
GF600	0.06	0.67	46.3
KP300	8.8	1.12	48.3
KP600	4.4	0.75	30.8

*R_s – Sheet resistance

†ESR – Equivalent series resistance

- ESR is calculated from Galvanostatic Cycling (GC) at current density of 1.04 mA/cm^2
- ESR lower than other studies on aqueous supercapacitors
- Stable ESR over 2000 cycles
- Specific capacitance calculated from GC at current density of 0.52 mA/cm^2

Conclusions

- Nanographite-Nanocellulose suspensions are highly shear thinning (power law index ~0.15)
- Slot-die coating can be used to coat such suspensions onto flexible substrates
- Coated electrodes have high porosity → benefits ion accessibility
- Calendering reduces electrode thickness and sheet resistance by at least 85% and 60% respectively
- CMC addition increases water retention; improves coatability but reduces conductivity

Future perspective

- Coating at higher solids to get thicker electrodes
- Influence of CMC and Nanocellulose addition on electrode performance and coatability
- Coating on metal foils – copper, aluminum and stainless steel
- Testing multi-cell supercapacitor assembly
- Targeting other applications such as:
  - Back contact for solar cells
  - Applications that require large area electrodes – floor sensors
  - Heat transfer applications – heated floors

Thank you

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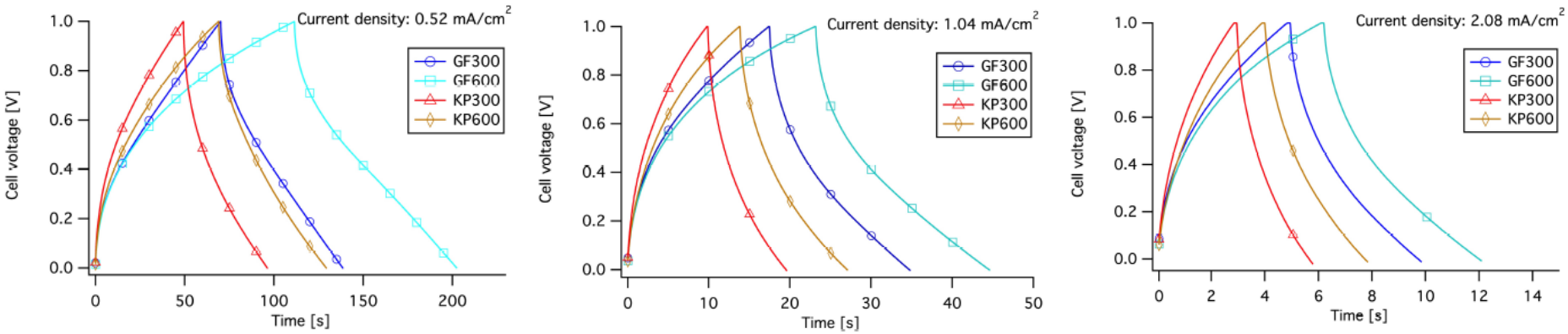
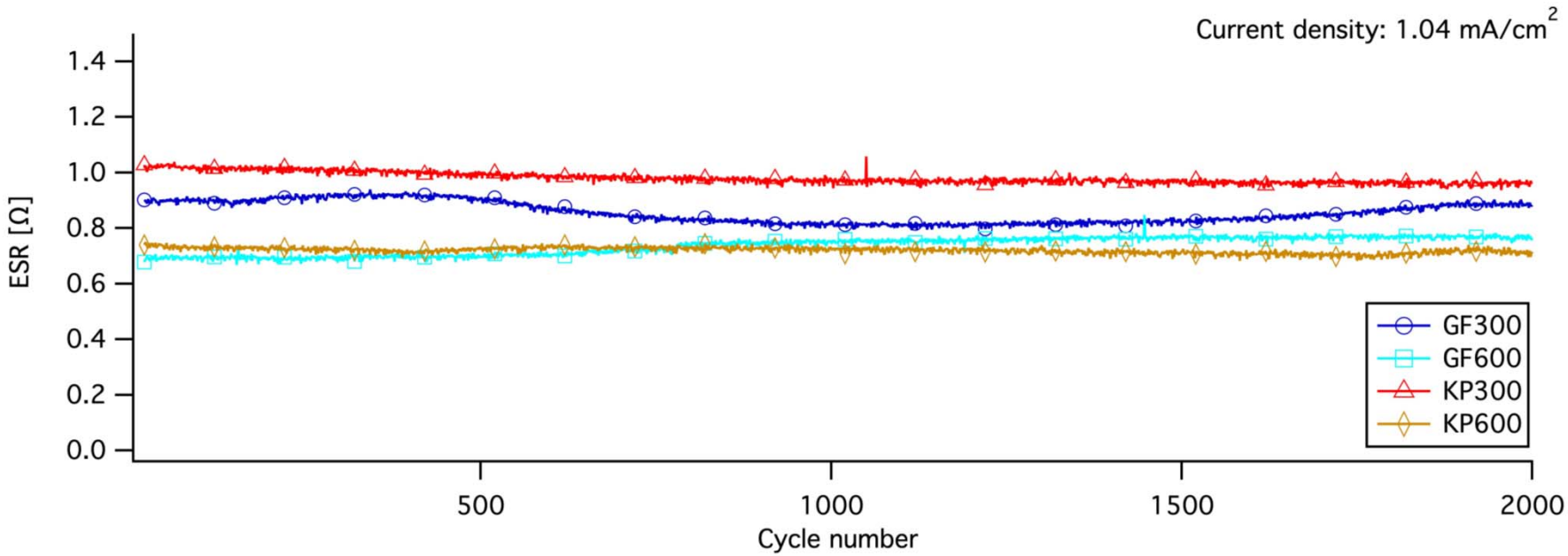
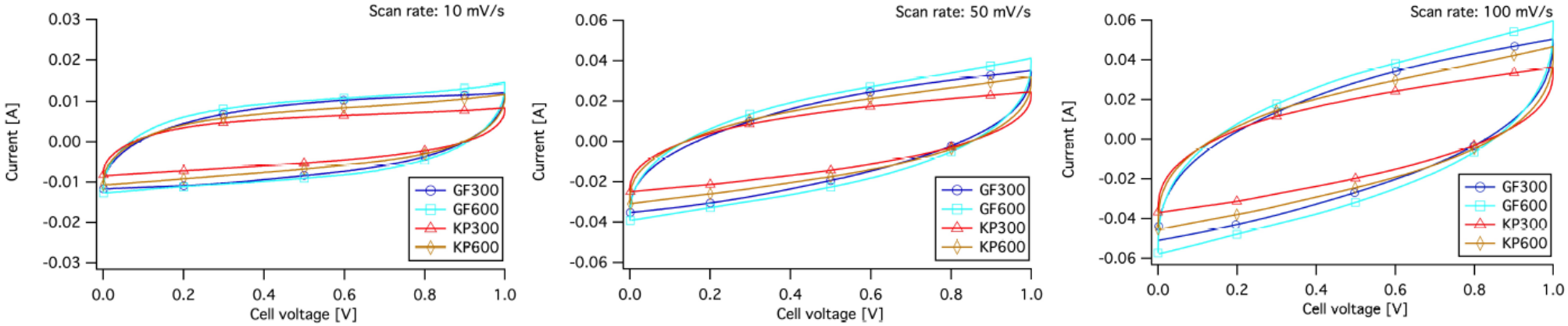
Galvanostatic cycling curves



ESR cycle stability curves



Cyclic voltammetry curves