Accelerating the Sluggish Kinetics in VRFBs with Carbon Nano Onions

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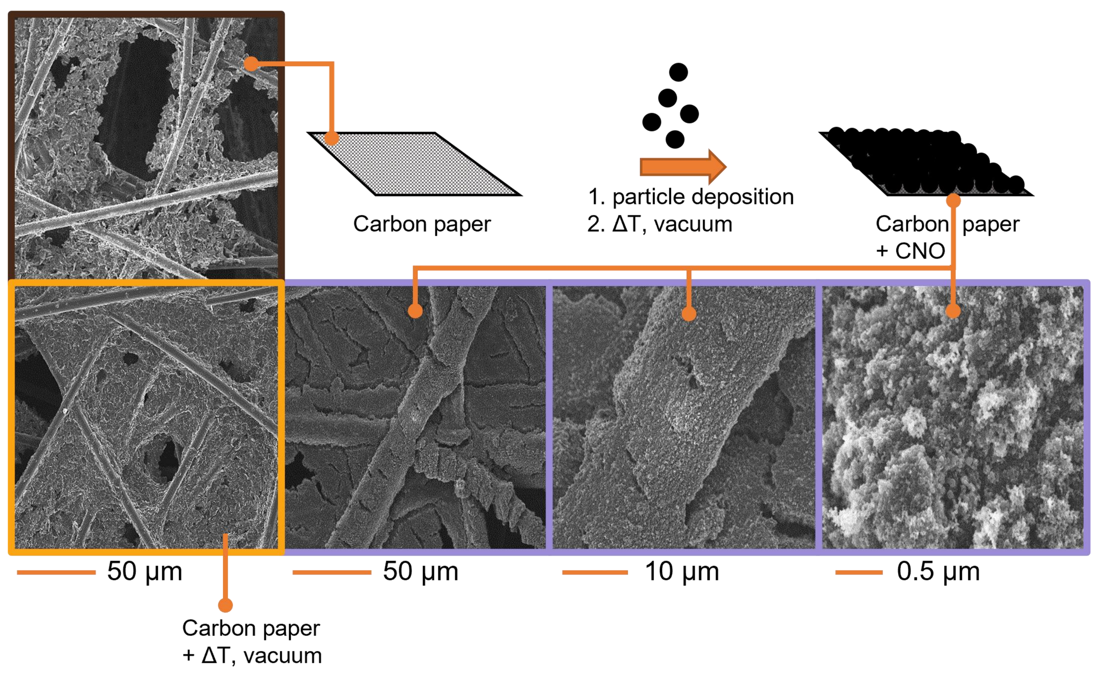
Motivation

New electrode materials required to enhance voltage efficiency and power density of VRFBs.

Material Preparation

SEM images before and after CNO deposition:

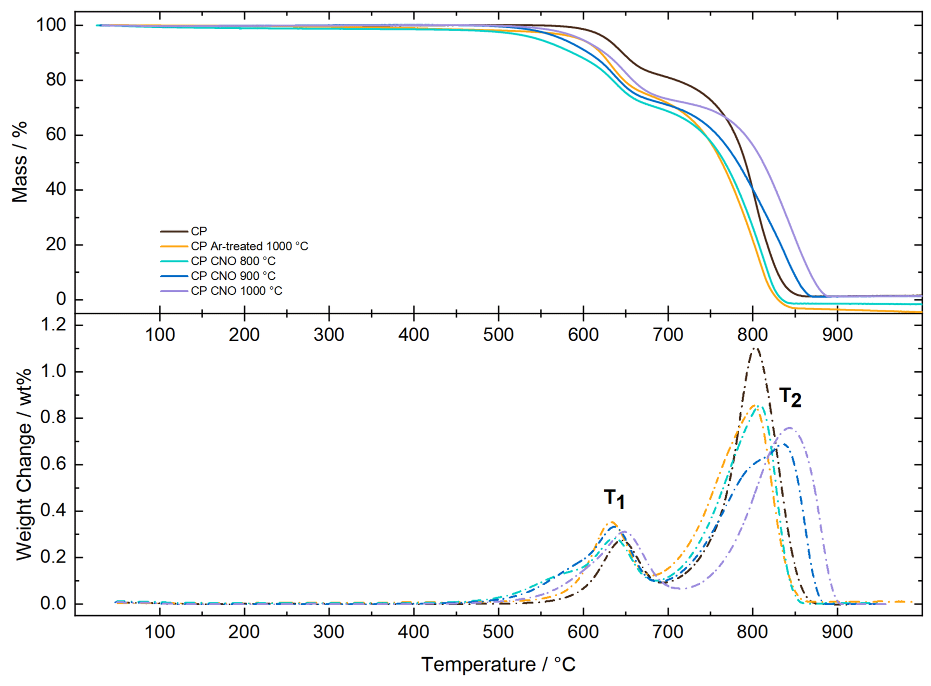


Plasma-enhanced chemical vapor deposition of carbon nano particles on carbon paper (CP) substrate [1].

Annealing in vacuum @ 800/ 900/ 1000 °C to obtain **carbon nano onions** (CNOs).

Composition

Thermogravimetric analysis



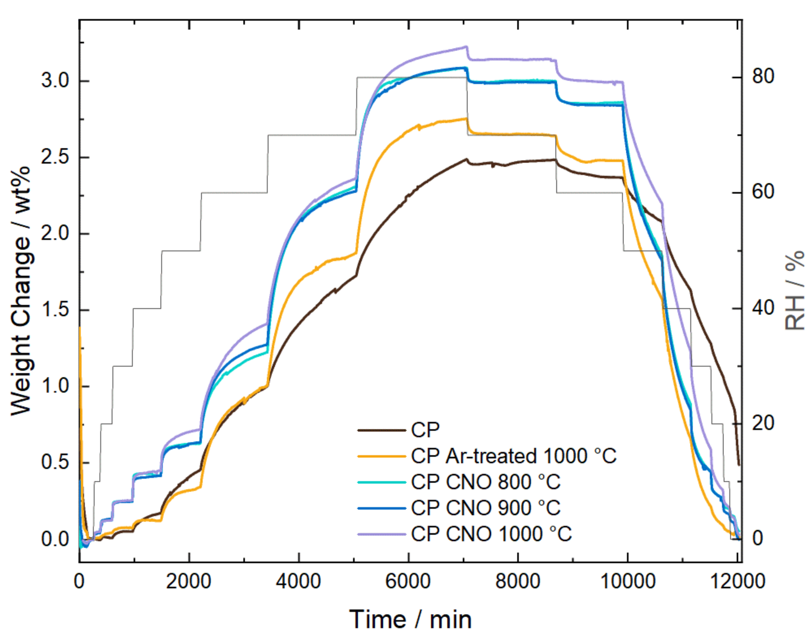
T_1 Oxidation of CNOs and CP binder components.

T_2 Oxidation of CP's carbon fiber components.

➔ Share of CNO approx. 4 – 4.5 wt%.
➔ Annealing leads to interconnection of CNOs.

Wettability

Dynamic vapor sorption



Stepwise increase and decrease of relative humidity (RH):

➔ Annealing of CP leads to improved hydrophilicity.
➔ CNO-coated materials show increased wettability.

Summary

CP substrates coated with CNOs and annealed at different temperatures were investigated for their use in VRFBs.

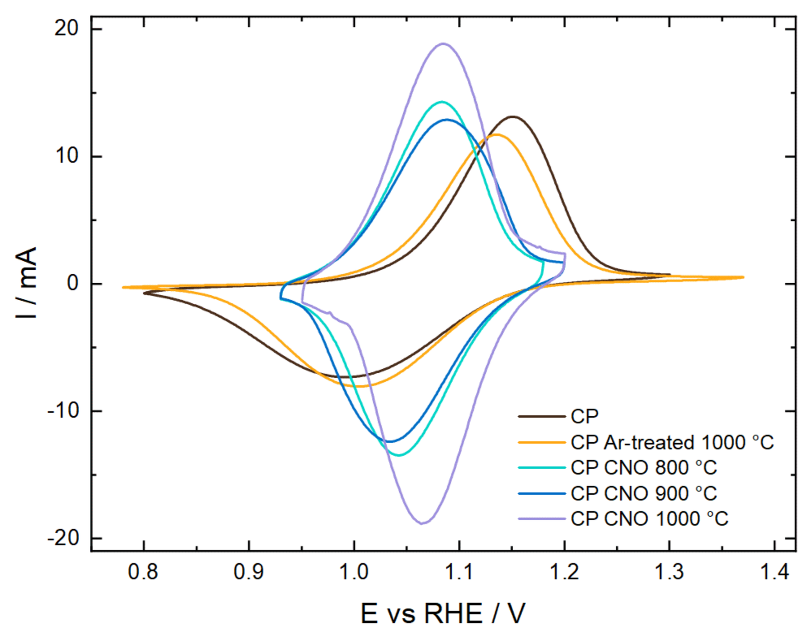
- The CNO's many defect sites lead to improved electrocatalytic capability and mass transport.
- Spots of mainly dispersive energy are beneficial for outer-sphere electron transfer, those with specific energy for inner-sphere [5].

➔ **Design process for an appropriate surface for the respective half-cell reaction must be carried out to optimize the electrodes performance.**

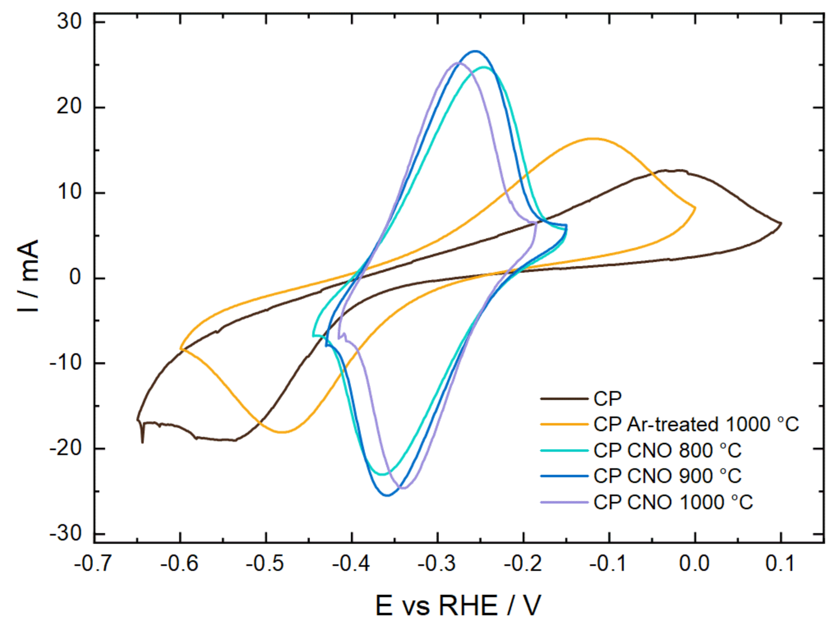
Electrochemical Performance

Cyclic voltammetry

Positive half-cell



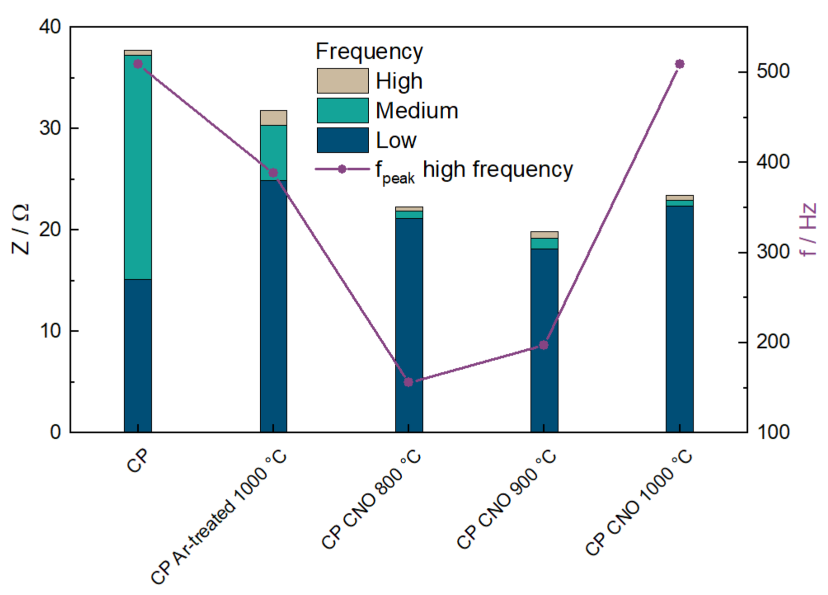
Negative half-cell



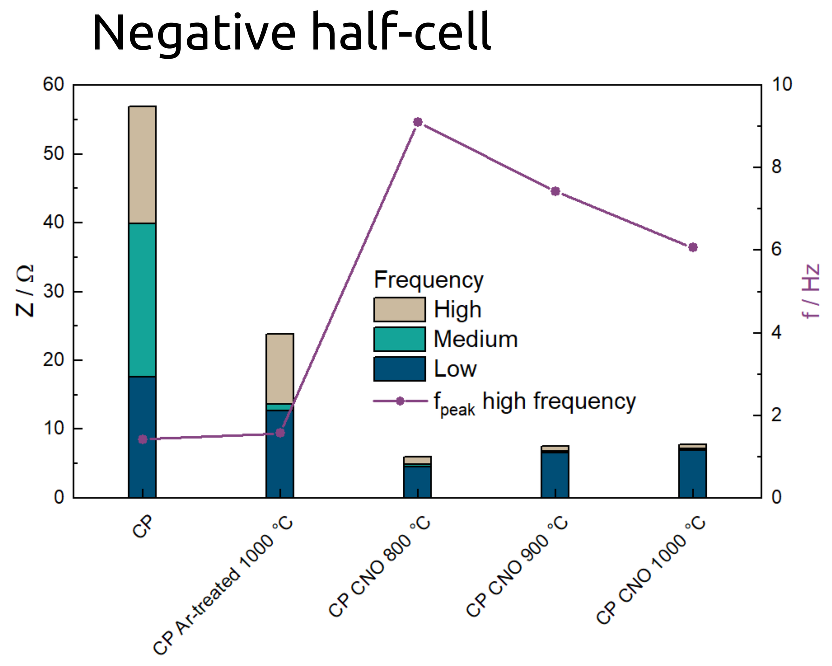
Superior performance of CNO-coated materials in both half-cells:
➔ High catalytic activity and reversibility.
➔ Improved diffusion.
➔ Increased peak currents.

Electrochemical impedance spectroscopy + Distribution of relaxation times analysis [2,3]

Positive half-cell



Negative half-cell

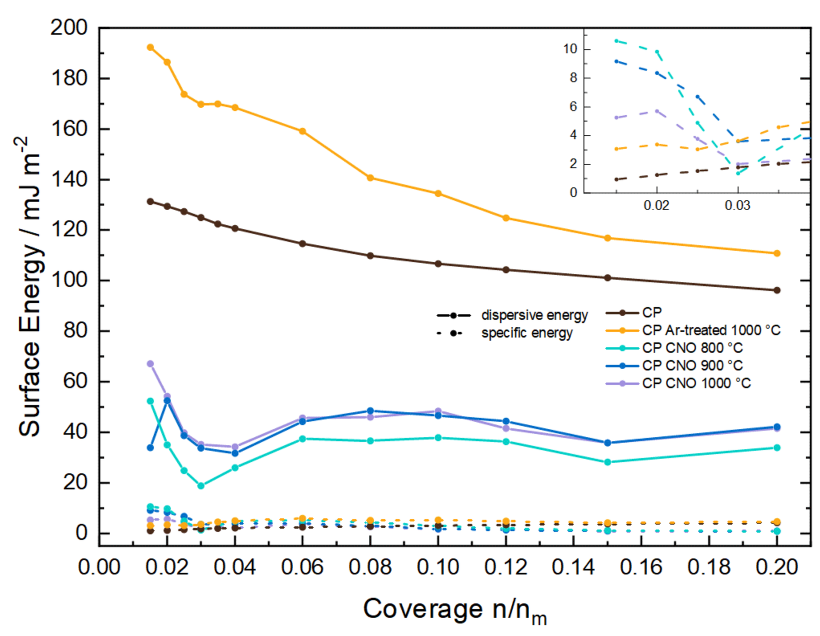


Low & medium frequency:
Improved viscous and diffusive transport. Affected by increased electrode compression due to additional CNO-coating [4].

High frequency:
Increased peak frequency of the rate-determining step.
➔ Controllable via annealing process.

Surface Energy

Inverse gas chromatography



- Determination of ***dispersive*** and ***specific*** surface energy.
- Normalized to the electrode's surface area previously determined using **BET method** with heptane.

➔ CP possesses almost exclusively dispersive energy.
➔ Annealing increases dispersive as well as specific energy.
➔ CNO-coating shields the underlying substrate.
➔ The level of energy is not decisive for the electrochemical performance of an electrode material.

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