Which Factors Govern the Long-Term Performance of OFB Electrodes?

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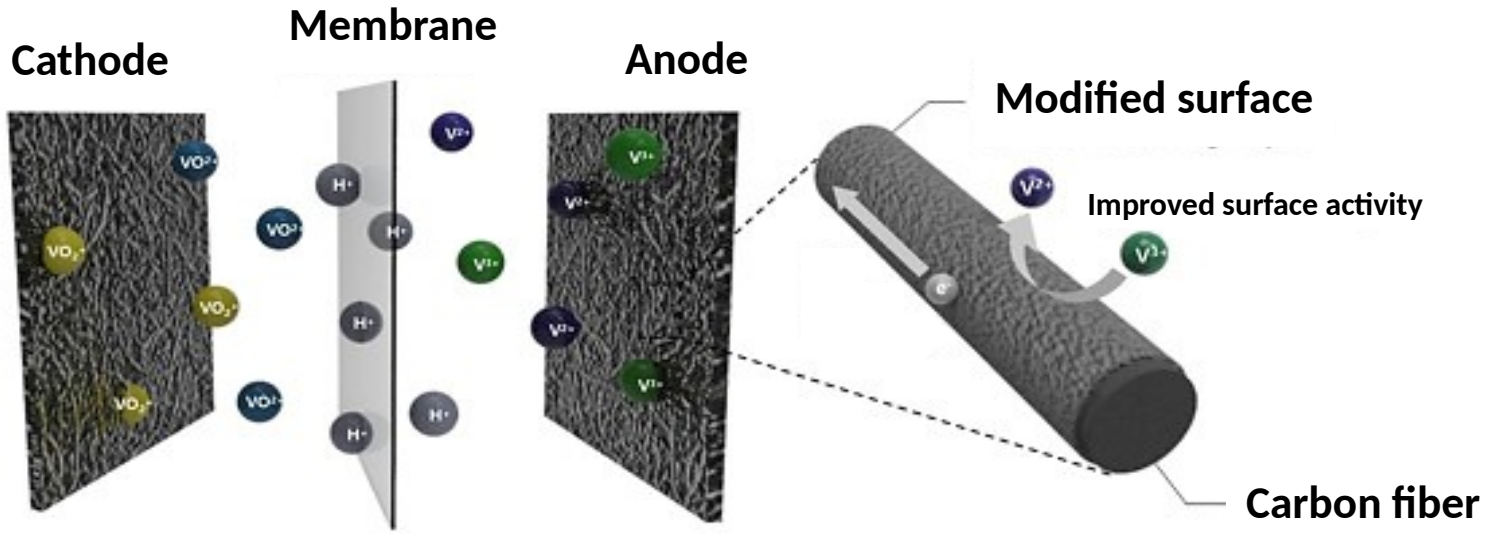
Move mountains

Role of Electrodes

- Electrical conductivity
- Chemical stability
- Provide electrochemical active sites
- Hydrophilicity → aqueous condition (Should it necessarily be hydrophilic?!)

Carbon felt (CF)



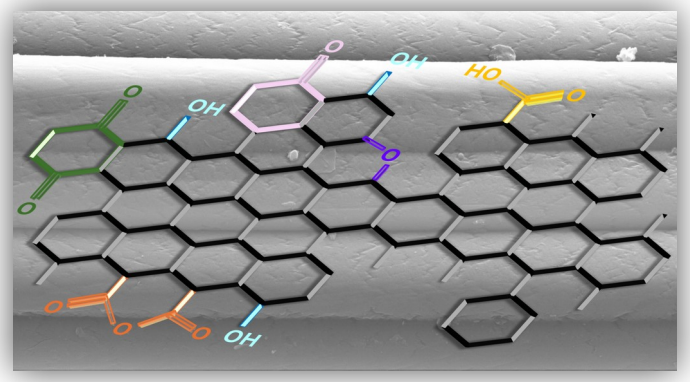
Problem statement and motivation

❑Shortcomings

- Poor hydrophilicity
- Low electrochemical activity
- Losing the performance over time → overoxidation; fouling; structural changes

❑Modification methods

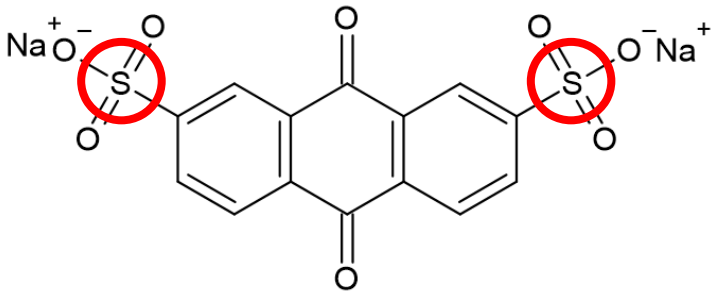
- Thermal treatment
- Plasma treatment
- KOH treatment
- CO_2 treatment
- Decoration with nanomaterials



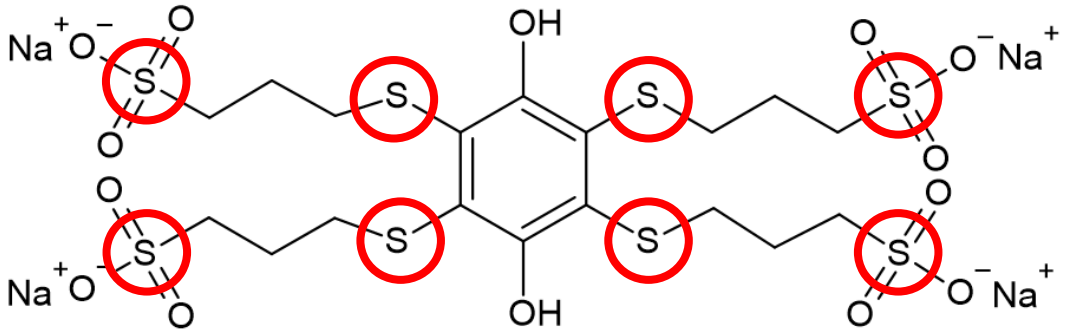
Fouling issue

Carbon felt electrodes are immersed in H_2SO_4 in which MHQS (positive electrolyte) and AQDS (negative electrolyte) are dissolved.

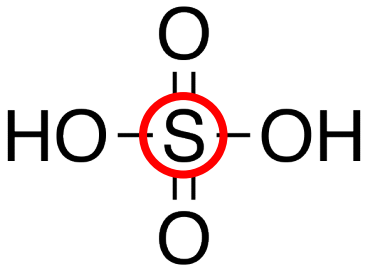
After tens to hundreds of battery cycles we detected **sulfur-based deposits** on carbon electrodes.
→ blocking active sites and reducing performance



AQDS



MHQS



Sulfuric acid

Electrode preparation

Pristine	O_2 Plasma	KOH	CO_2
Treatment As-received carbon felt Reference	**Treatment** RF plasma 200 W / 10 min Ambient temp.	**Treatment** 5 M KOH aq. 800°C / 1 h (N_2 atmosphere)	**Treatment** CO_2 gas 975°C / 2 h
Mechanism No treatment Baseline performance	**Mechanism** Surface oxidation via reactive O species; High O/C ratio	**Mechanism** Alkaline gasification; O-functionalization $6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3$	**Mechanism** Selective deep etching; minimal surface functionalization $C + CO_2 \rightarrow 2CO$
Characterization C: 97.5 at.% O: 1.7 at.% SSA: 0.9 $m^2.g^{-1}$	**Characterization** C: 81.4 at.% O: 17.1 at.% SSA: 1.1 $m^2.g^{-1}$	**Characterization** C: 90.7 at.% O: 9.3 at.% SSA: 11.0 $m^2.g^{-1}$	**Characterization** C: 96.4 at.% O: 2.9 at.% SSA: 46.7 $m^2.g^{-1}$

Raman spectroscopy

G band → graphitic
D band → defect

- **Total disorder indicator (S):**

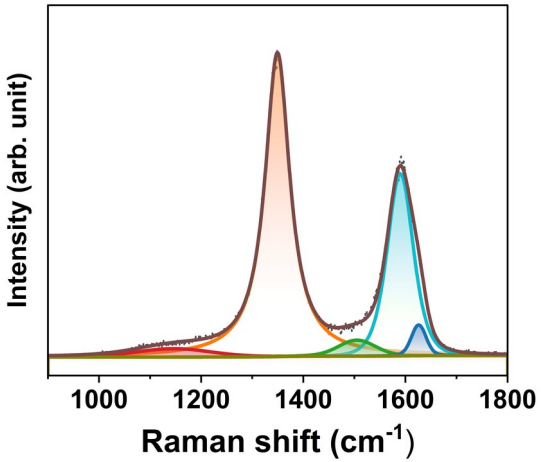
$$S = \frac{A_{D_{tot}}}{A_G} = \frac{A_D + A_{D3} + A_{D4}}{A_G}$$

- **Defect-type indicator (I):**

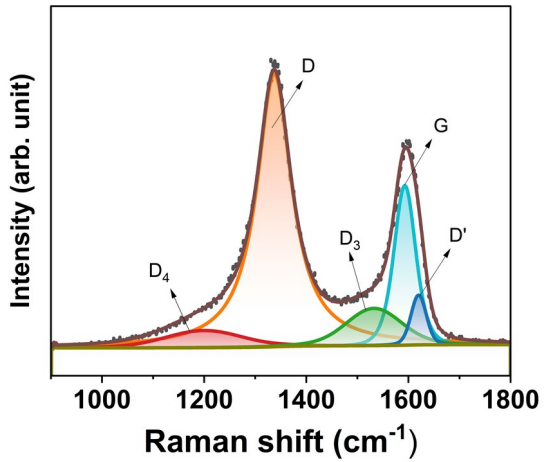
$$I = \frac{I_D}{I_{D'}}$$

≃13 → sp^3 hybridization
≃7 → vacancy-like defects
≃3.5 → boundary-like defects

Pristine



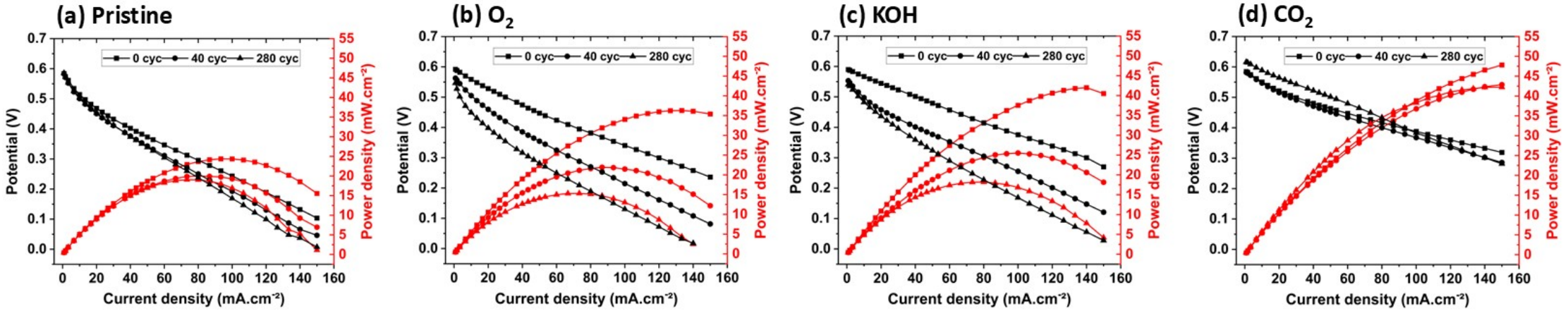
CO_2 treated



Electrode	S	I
Pristine	2.5	9.9
O_2 plasma	4.1	7.2
KOH	3.3	8.8
CO_2	4.7	5.6

CO_2 treatment : increase in **structural defects** and producing **vacancy** and **boundary (edge)** defects

Polarization assessment of pristine and treated carbon electrodes for ORFB



	ASR (Ω.cm^2)			R_{ct} (Ω.cm^2)			i_0 (mA.cm^{-2})		
	0	40	280	0	40	280	0	40	280
Pristine	2.6	3.1	3.4	6.1	9.0	9.0	2.1	1.4	1.4
O_2	2.2	2.8	3.1	1.6	4.3	14.5	8.0	3.0	0.9
KOH	2.1	2.4	3.2	0.4	4.7	3.6	31.3	2.7	3.6
CO_2	1.5	1.7	2.3	2.6	2.1	0.6	5.0	6.1	22.2

CO_2→ lowest ASR prior and after cycling

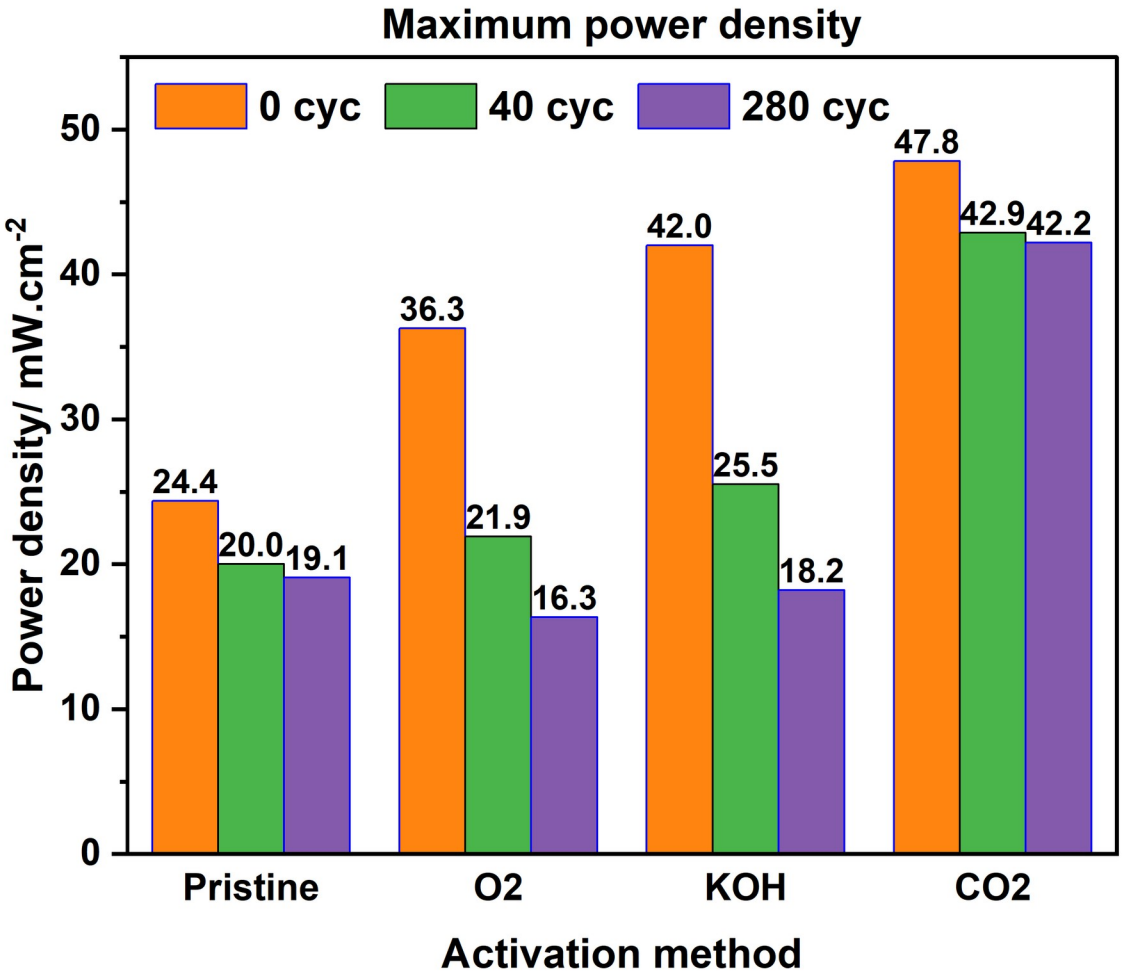
KOH→ lowest R_{ct} prior to cycling

CO_2→ lowest R_{ct} after cycling

The kinetic improved in CO_2 (self-activation)

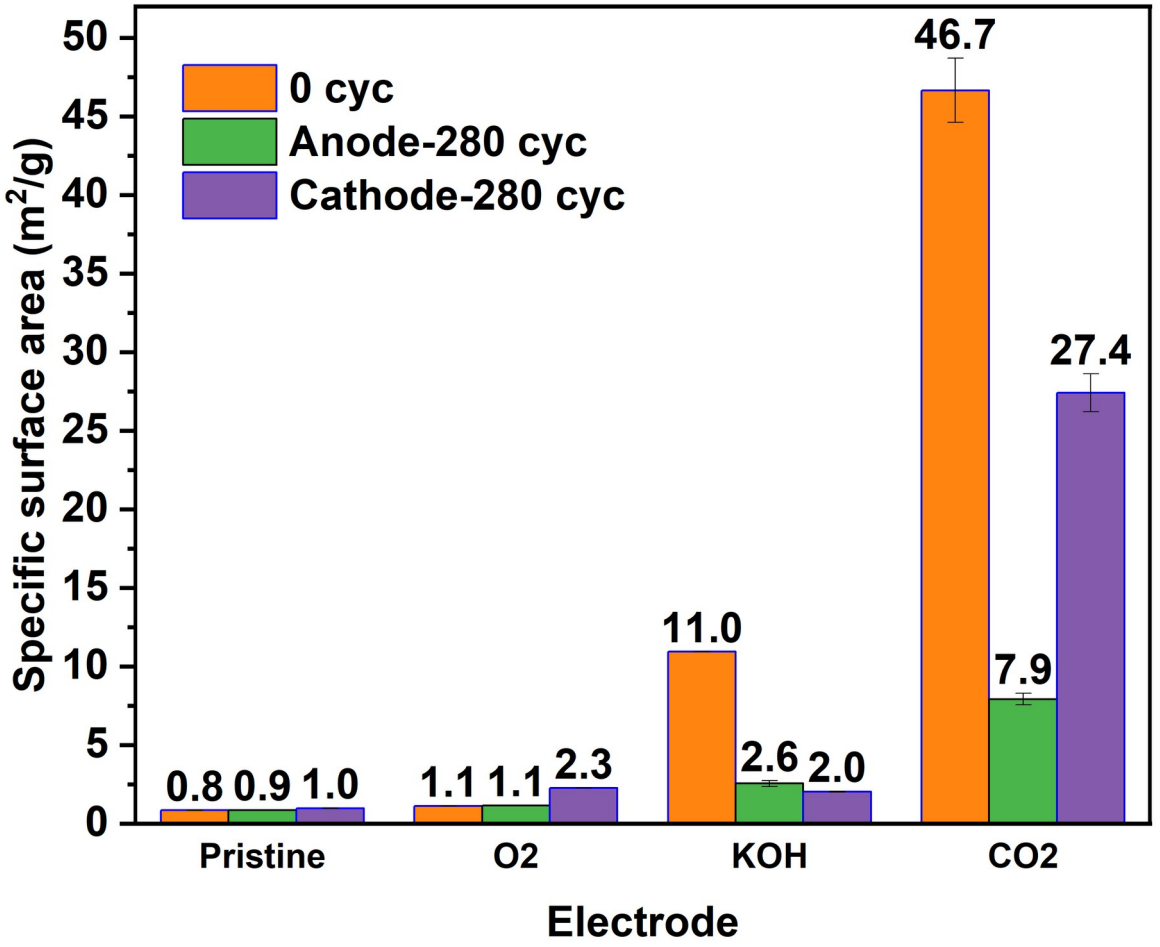
Is fouling the dominant limiting factor?

- Considerable amount of **O (15-25 at.%)** and **S (2-7 at.%)** detected on electrodes.
- CO_2 → less pronounced
- Pristine, O_2 plasma and KOH treated electrodes experienced severe performance decrement.
- **CO_2** treated electrodes maintain performance, indicating **fouling isn't the sole limiting mechanism**.



Specific surface area changes

- O_2-plasma: Slight increase vs. pristine
- **KOH**: Strong initial increase → significant drop after cycling
- CO_2: Remarkable increase; decreases after 280 cycles but remains higher than others



Why do CO_2-treated electrodes perform better?

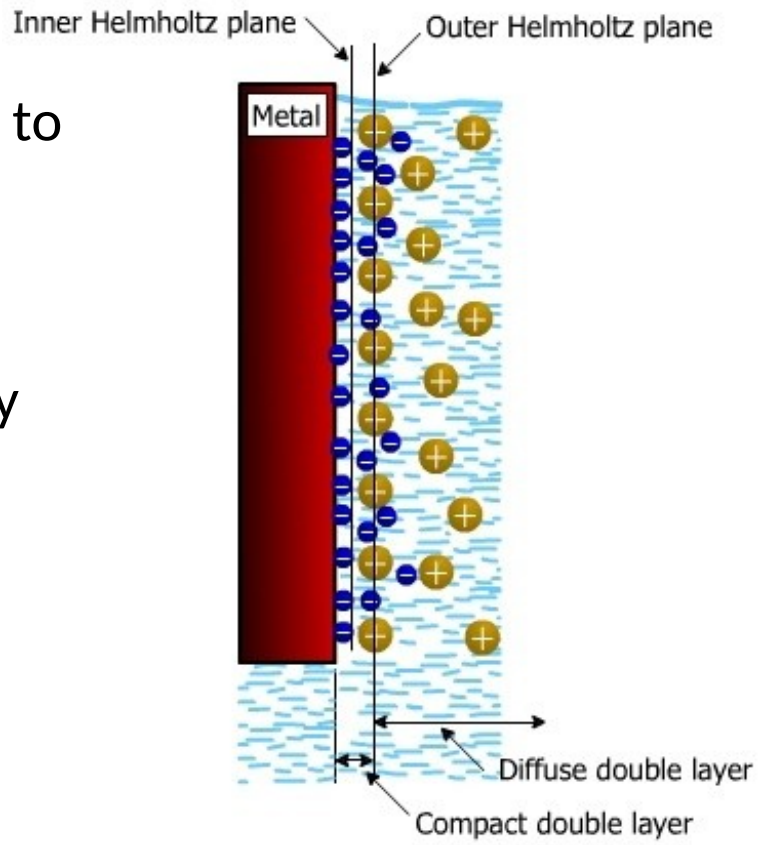
Outer sphere → tunnelling between the electrode and redox molecule
Inner sphere → interaction between the analyte and the surface

Hydrophilicity issue:
Water molecules increase the distance for active materials (MHQS/AQDS) to reach the electrode surface →quenching tunneling

Advantage of hydrophobicity + high surface energy:
Reducing the thickness of the double layer → higher double layer capacity and lower overpotential

The high surface energy attracts the active materials more efficiently. And **antenna effect** may play a role due to presence of nanoporosity.

Less contact with acid also can explain the lower degradation.



Conclusion

- **O_2 plasma**, **KOH** and **CO_2** treatment **enhanced performance initially**, while O_2 plasma and KOH treated electrodes performance dropped to even lower than pristine electrode after 280 cycles.
- **Fouling** was **universal** across all electrodes, while it was more pronounced on pristine ones and less on CO_2 treated electrodes.
- **CO_2-treatment** enhanced the **surface area** more than **4-folds** compared to other treatments
- **CO_2-treatment** increased the overall **lattice disorder** and produced **vacancy** and **boundary (edge)** defects as the preferential active sites.

 Hydrophobicity and **high surface energy** of CO_2 treated electrodes may enable the quantum tunneling effect → superior long-term performance of them.

 Surface chemistry, structural defect type and density, as well as **surface area and energy** are the main parameters governing the electrodes performance in flow batteries.

Acknowledgement

THANK YOU FOR YOUR ATTENTION!

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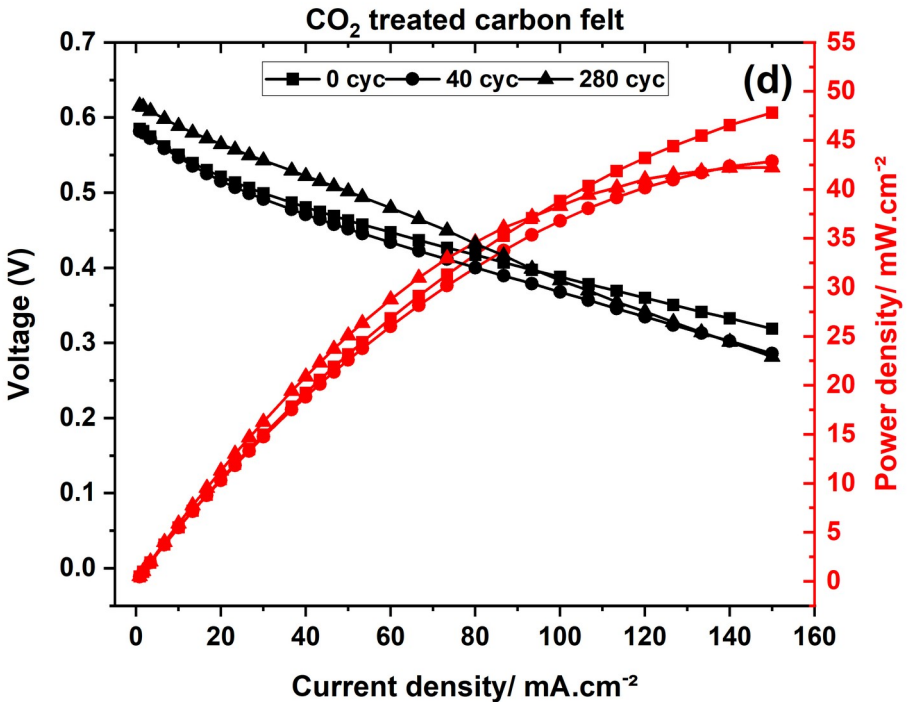
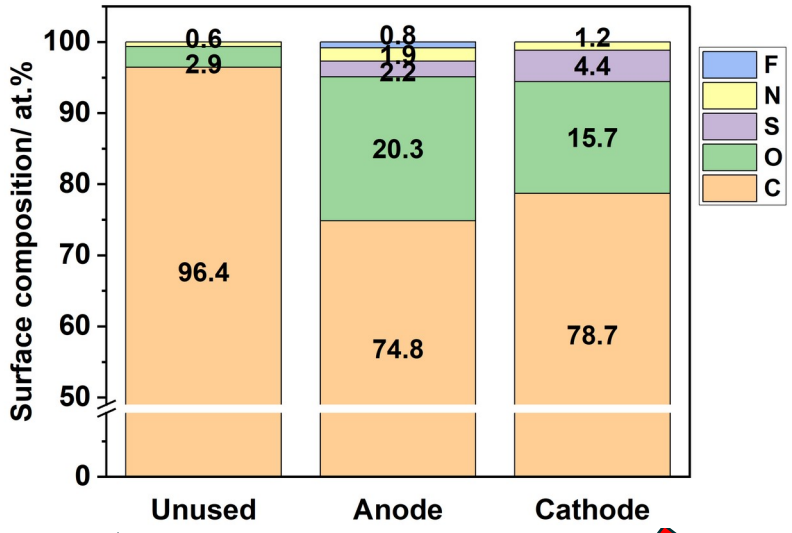
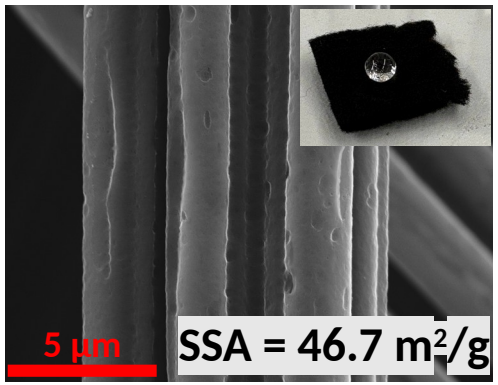
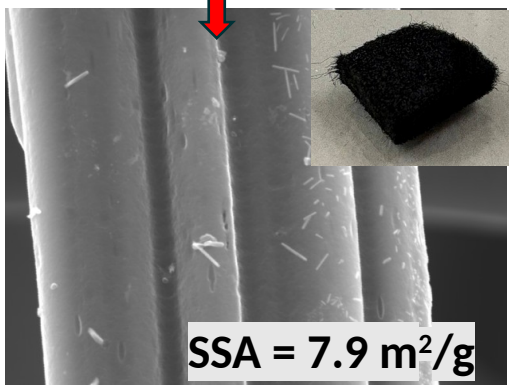
CO_2 treated carbon felts

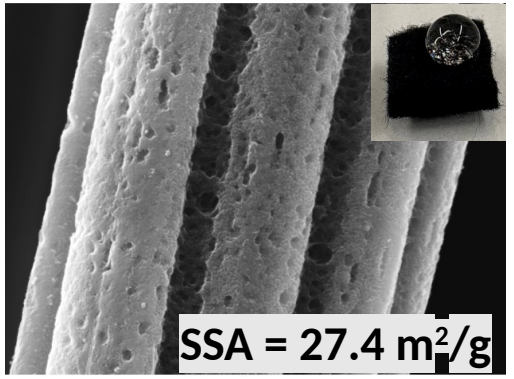
- **CO_2** activation delivered the highest and most stable power density **despite hydrophobicity** and fouling.
- Higher surface area compared to other methods could be the reason for superior performance.





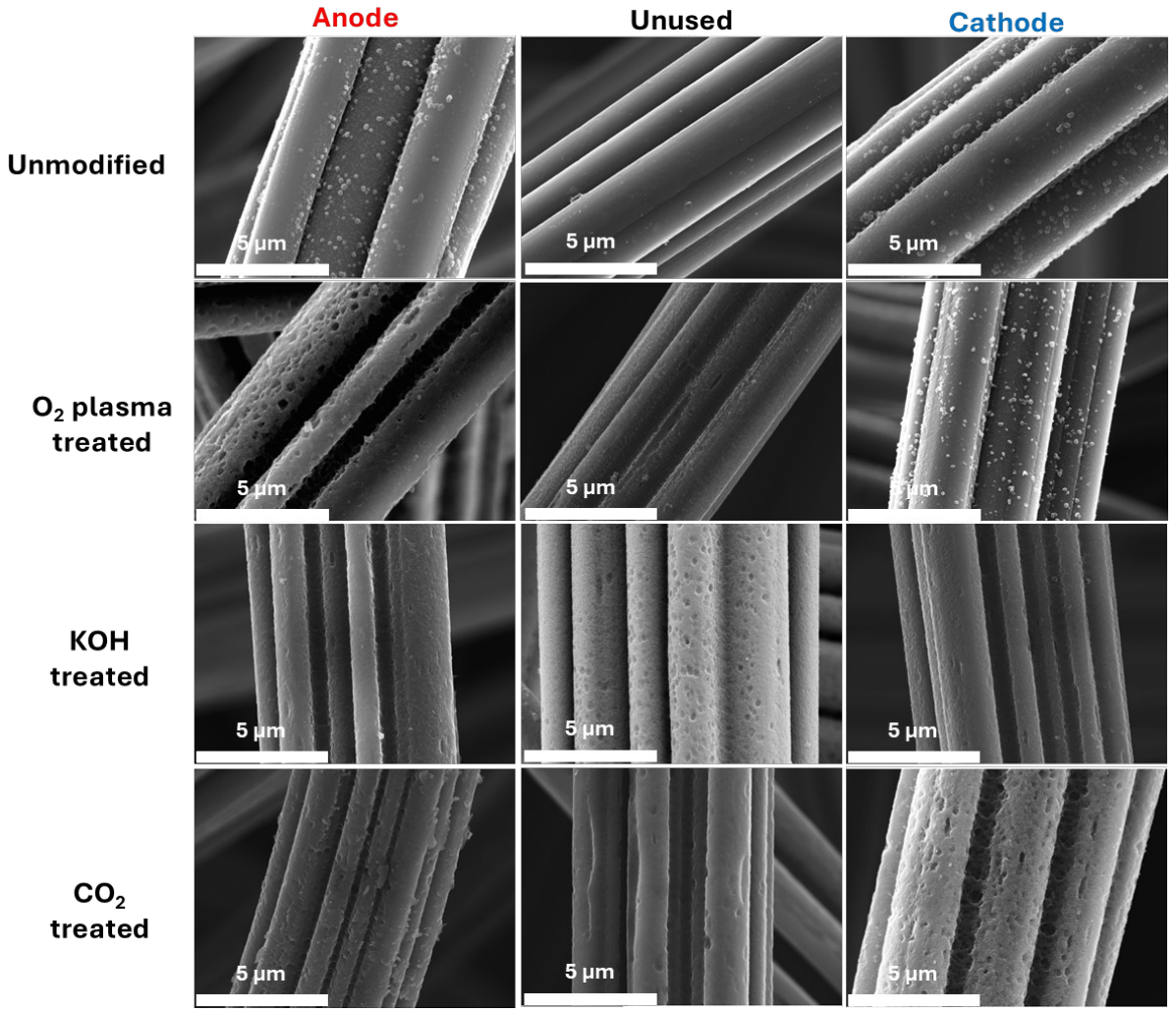






Morphology of electrodes (280 cycles)

- Modifications altered the morphology of the carbon fibers.
- Not the same morphology on anodes and cathodes. Spherical and needle-like particles, as well as porous structure can be seen.



Surface energy (iGC) of pristine and CO_2 activated carbon felts

Specific surface energy:
polar interactions → wettability

Dispersive surface energy:
non-polar/Van der Waals → surface area (porosity)

Slope of dispersive energy:
High → heterogenous surface
Low → uniform surface