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# Hierarchical Porosity in Electrospun Capacitive Deionization Electrodes

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# Introduction – The Water Problem

- Over 2 billion people lack access to safe drinking water[1]
- Over 3 billion people live in agricultural areas with water scarcity[2]
- Only 2.5% of the Earth's water is fresh water[3]
  - Nearly 70% of that freshwater is inaccessible in glaciers and ice caps
- Water scarcity is increasing over time
- New practices and technologies must be developed

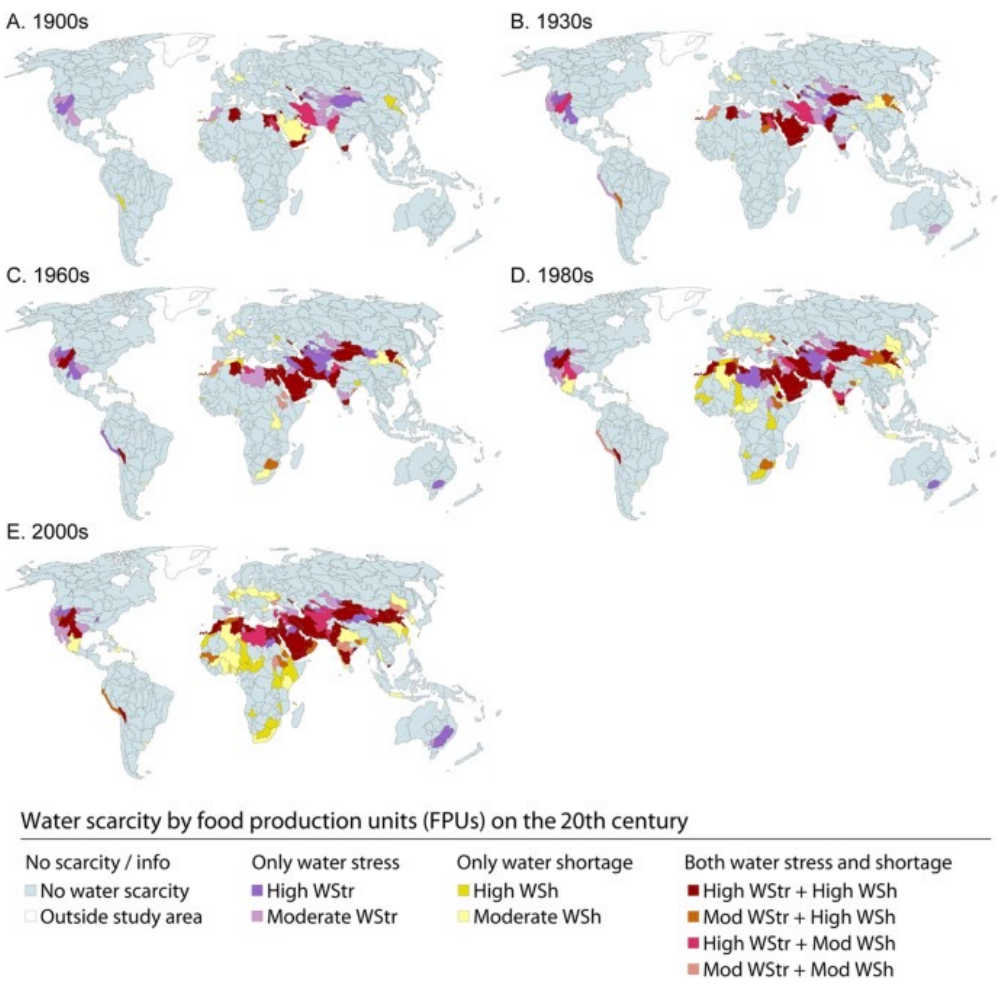



Fig 1: Global water scarcity and shortages over time.[4]



1. UN, Global Issues - Water
2. Food and Agriculture Organization of the United Nations. Status of Water Shortages and Scarcity in Agriculture. 2020.
3. USGS, Where is Earth's Water?
4. Kummu, M., Guillaume, J. H. A., de Moel, H., Eisner, S., Flörke, M., Porkka, M., Siebert, S., Veldkamp, T. I. E., & Ward, P. J. (2016). *Scientific Reports*, *6*(1), 38495. https://doi.org/10.1038/srep38495

# Current State of Desalination

- Reverse Osmosis (RO) accounts for nearly 70% of operating desalination plants (2019)
  - Est ~16,000 plants
- Seawater accounts for 61% of water desalinated
- Brackish water accounts for 21%
  - And increasing
  - RO not as efficient for BW

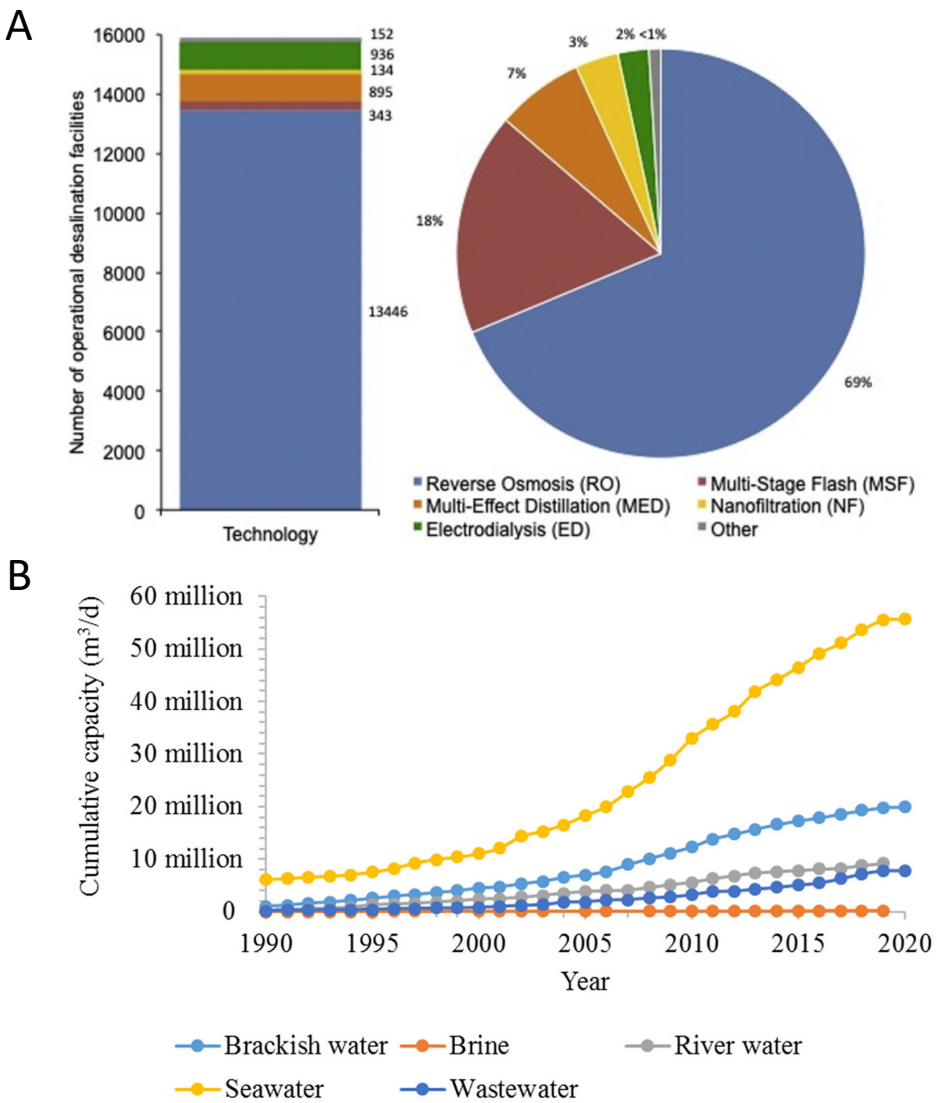



Fig 2A: Number of operational desalination facilities for each technology. B) Capacity of desalination for different feed streams.


1. Jones, E., Qadir, M., van Vliet, M. T. H., Smakhtin, V., & Kang, S. mu. (2019). *Science of the Total Environment*. https://doi.org/10.1016/j.scitotenv.2018.12.076
2. Eke, J., Yusuf, A., Giwa, A., & Sodiq, A. (2020). *Desalination*, *495*, 114633. https://doi.org/10.1016/J.DESAL.2020.114633

# Background – Capacitive Deionization (CDI)

- Surface driven process
  - Electric double layer
- Symmetrical electrodes
  - High surface area carbons
- Brackish water (< 2000 ppm TDS)
- Cyclical operations
  - Charge – Adsorption
  - Discharge – Desorption
- Things to improve on:
  - Capacity
  - Rate
  - Lifetime

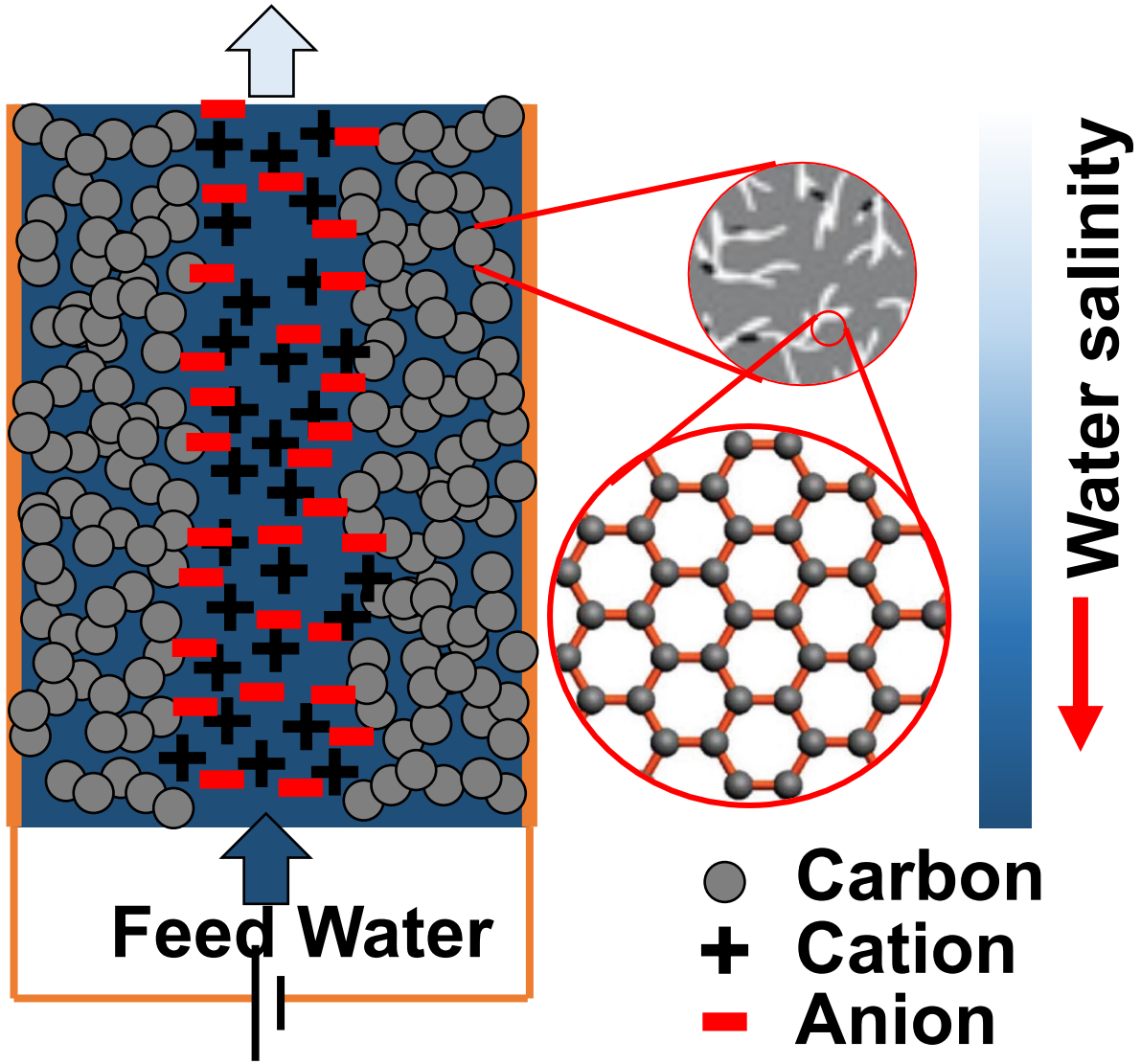



Fig 3: Schematic of CDI operation

# Background - Electrospinning

- Electrospinning as a template for modifications
  - High tunability
  - High macroporosity
- Ink composition
  - Wt% of solids and additives, solvent choice
- Electrospinning conditions
  - Voltage, flow rate, tip to collector distance
- Polyacrylonitrile (PAN) used for all fibers (Fig B)
  - Easily electrospun
  - High carbon yield
- Carbonized at 800-1000°C under $N_2$ (Fig C, D)

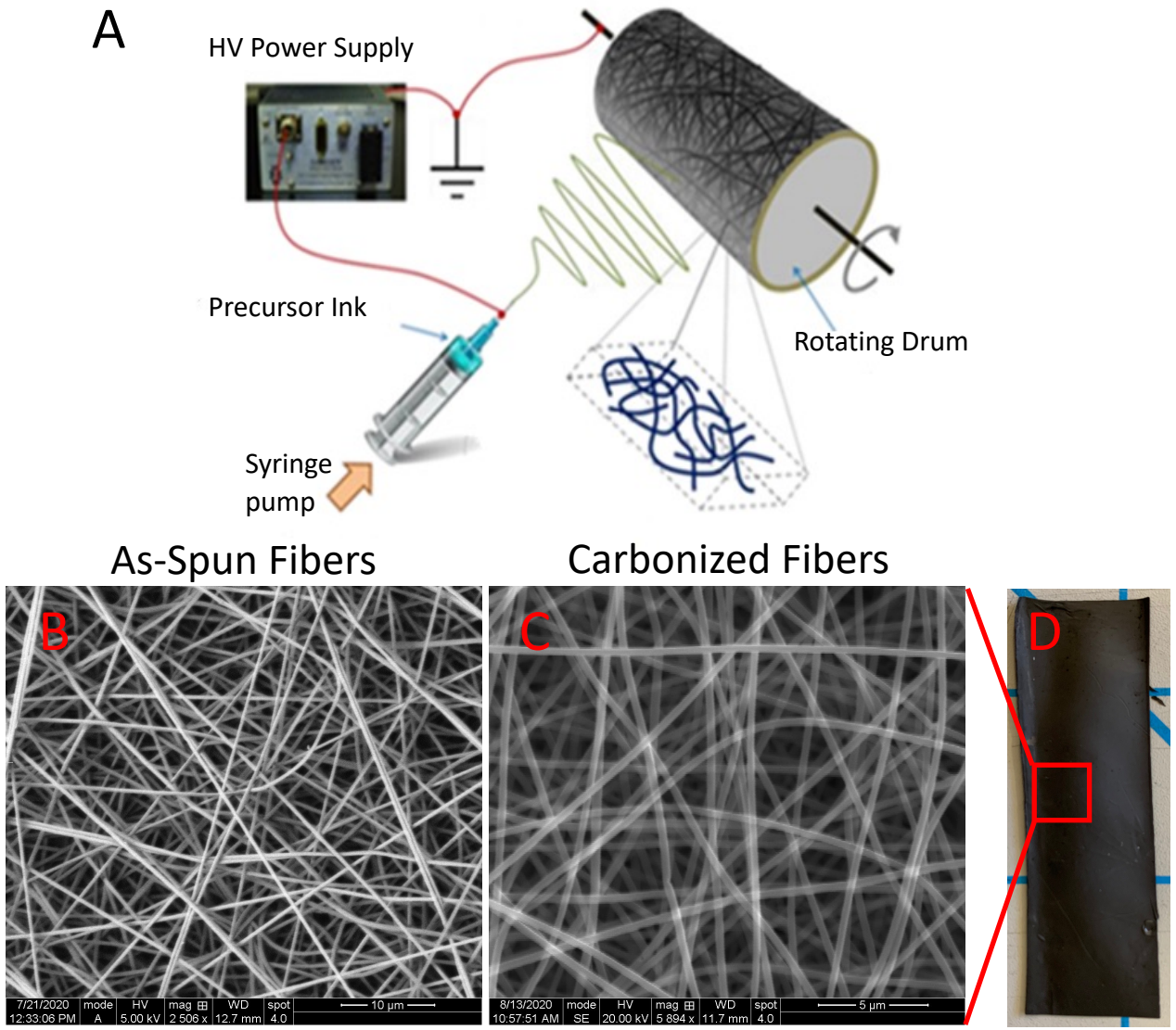



Fig 4: A) Schematic of a typical electrospinning apparatus. B) Electrospun PAN fibers. C) Carbonized PAN fibers. D) Photo of carbonized PAN mat.

# Hierarchically Porous Nanofiber Fabrication



- Goal: Create a pore "highway" to enable electrodes with
  - High SSA/SAC
  - High SAR
- Mesoporosity –Sacrificial Pore Formers
  - $SiO_2$
    - NaOH
- Microporosity - Etchants
  - KOH

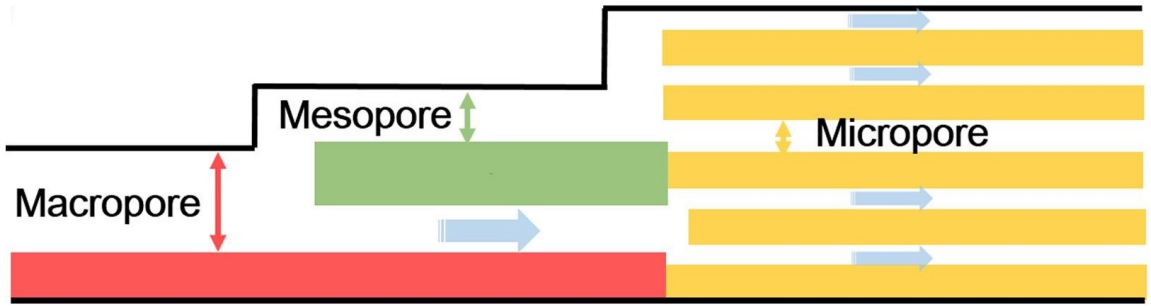


Fig 5: Schematic of hierarchical porosity[1] and example hierarchically porous carbon[2].

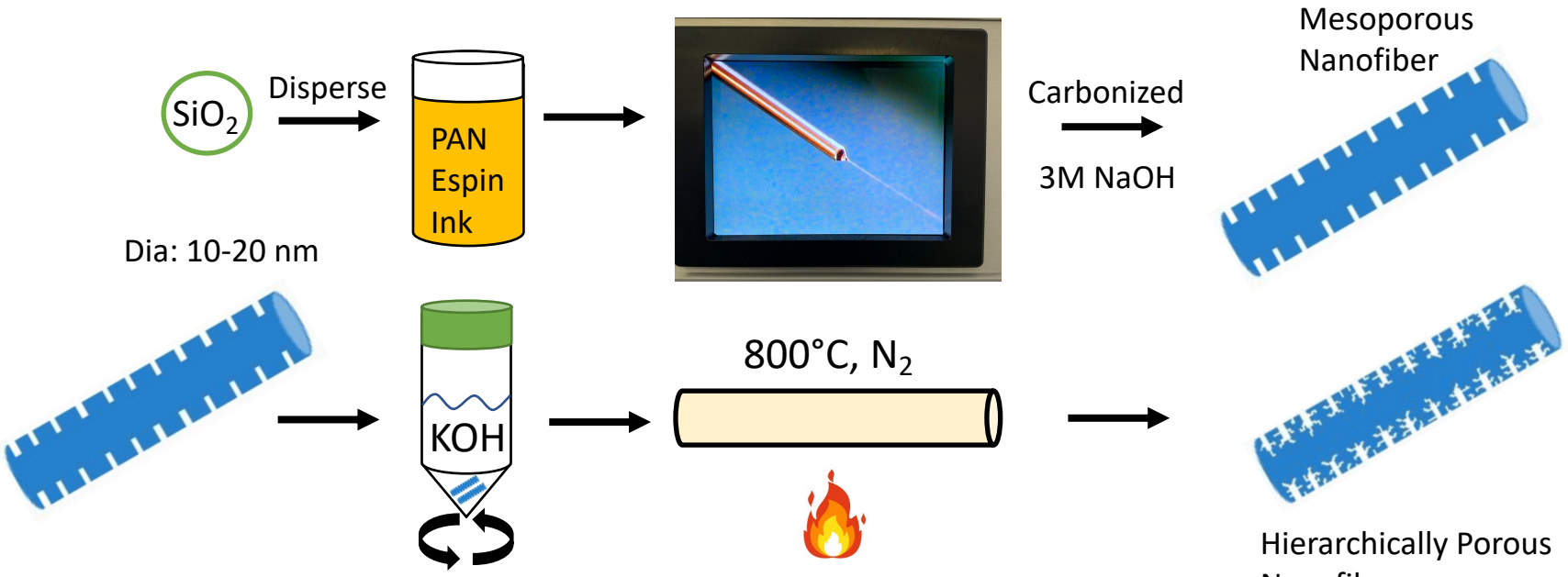



Fig 6: Schematic of hierarchically porous nanofiber fabrication.

1. Han, B., Cheng, G., Wang, Y., & Wang, X. (2019). *Chemical Engineering Journal*.
2. Noked, M., Avraham, E., Soffer, A., & Aurbach, D. (2009). *Journal of Physical Chemistry C*. https://doi.org/10.1021/jp905987j

# Imaging of Etched Nanofibers

- Fibers maintain structure post etching
- Pores are randomly distributed, but every fiber is highly porous
- KOH treatment increases surface roughness

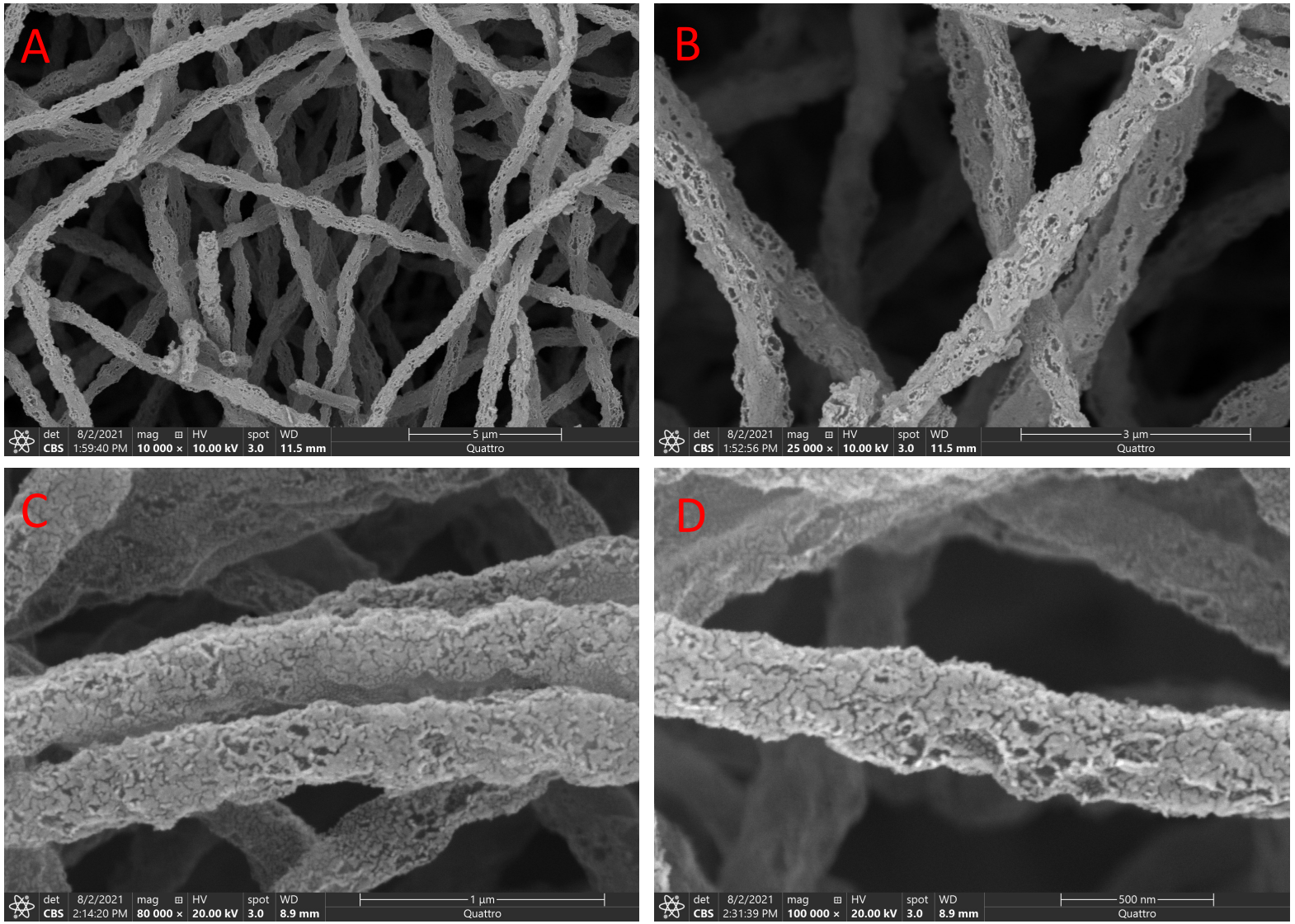
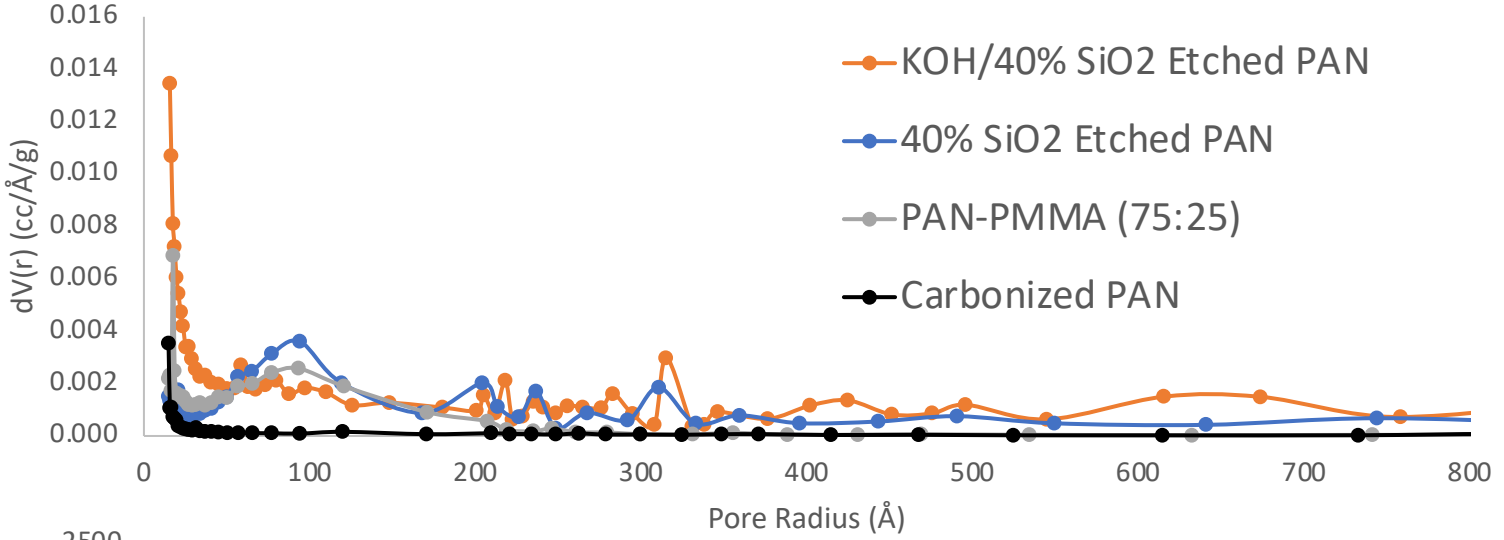



Fig 7: SEM of etched nanofibers. A, B: 40% $SiO_2$ Etched PAN. Fig C, D: 40% $SiO_2$, KOH etched PAN

# Inducing Hierarchical Porosity

- Silica etching effective at inducing mesoporosity, with the most pores at 9nm
  - PMMA pore formation creates both meso- and microporosity, leading to higher SSA, but lower pore volume than $SiO_2$ etching
- > 97% of $SiO_2$ is removed, via XRF
- KOH etching is effective at creating micropores and increasing pore volume

| Sample | SSA ($m^2/g$) | Pore Volume (cc/g) |
|---|---|---|
| Carbonized PAN | 69 | 0.085 |
| PAN-PMMA (25%) | 475 | 0.371 |
| 40% SiO2 | 175 | 0.91 |
| 40% SiO2, 7:1 KOH | 936 | 1.844 |
| 40% SiO2, 10:1 KOH | 1374 | 2.254 |



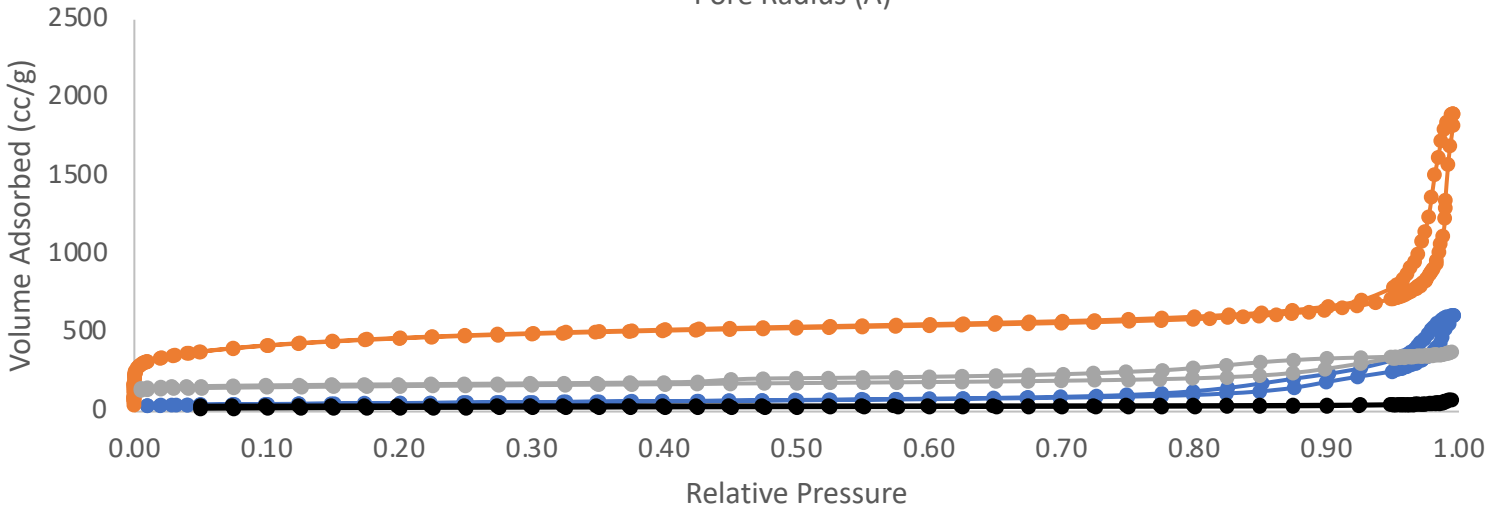




Figure 8: A) BET pore size distribution of various fiber samples: Carbonized PAN (no etchants), PAN-PMMA (75:25), PAN etched by 40% $SiO_2$, and PAN etched by 40% $SiO_2$ then 10:1 KOH. A) Mesopore distribution. B) Adsorption/desorption isotherms.
Legend applies to both A and B.

# Preliminary Work – Electrochemical Analysis

- Cyclic voltammetry done in 1M NaCl
- Electric double layer increases post $SiO_2$ removal and further upon KOH etching
- Higher scan rates increase resistance due to large micropore volume

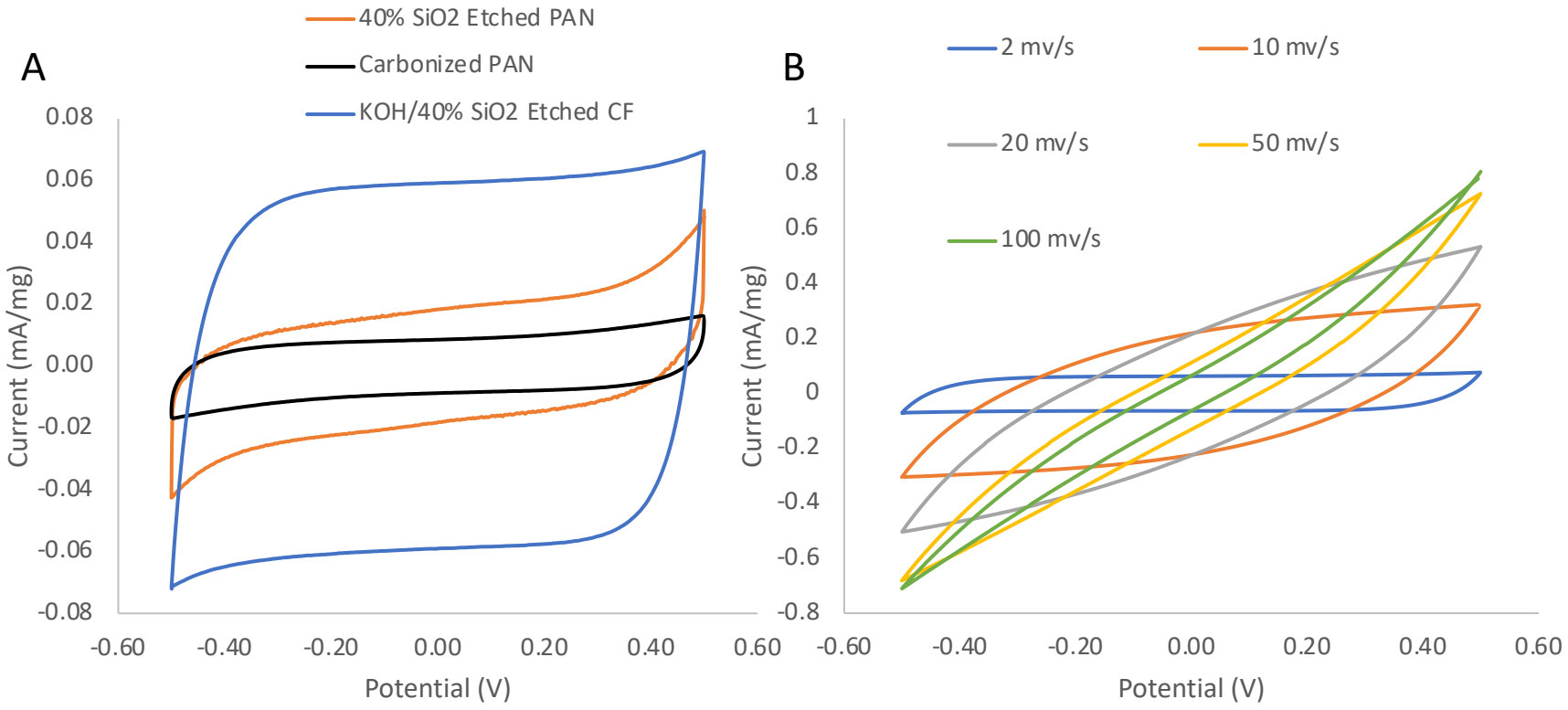



Figure 9: Cyclic voltammetry between -0.5V and 0.5V, in 1M NaCl of A) KOH and 40% $SiO_2$ etched PAN, 40% $SiO_2$ etched PAN, and non-etched carbonized PAN, 2 mv $s^{-1}$ scan rate. B)KOH and 40% $SiO_2$ etched PAN at varying scan rates.

# CDI Performance

- 10:1 KOH:CF mass ratio, 40% $SiO_2$-etched PAN
- 5 mins charge (1.2V), 30 mins discharge (0V)
- 500 ppm NaCl

- Achieves a peak SAC of 13.4 mg $g^{-1}$
  - Over 5x that of only-$SiO_2$ etched PAN
    - (2.8 mg $g^{-1}$)
  - Over 6x un-etched PAN
    - (~1.9 – 2 mg $g^{-1}$)

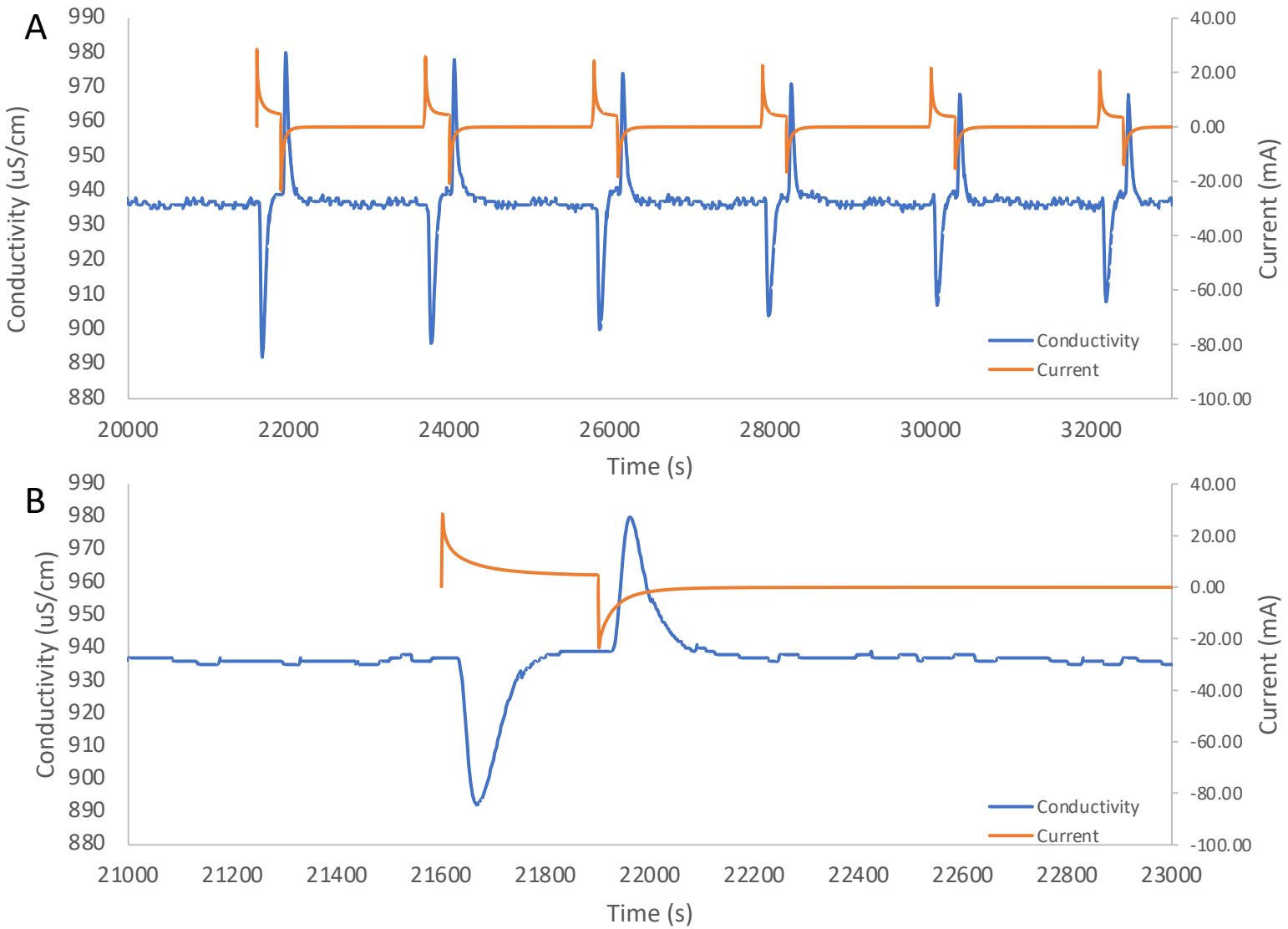



Figure 10: Constant voltage desalination using KOH/$SiO_2$ etched nanofibers. A) Conductivity vs time cycling. B) First charge and discharge cycle

# Summary/Future Work

- Hierarchical Porosity Generation
  - $SiO_2$ as a mesopore former
  - KOH as a micropore etchant
  - High SSA, high SAC materials

- Tune $SiO_2$ wt.% in conjunction with KOH ratio to achieve variable mesopore/micropore volume fractions

- Determine optimal mesopore volume %
  - Percent of total pore volume that is mesopores