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# Variable Phase and Electrochemical Capacitance of Electrospun MnOx Fibers

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# Variable Phase and Electrochemical Capacitance of Electrospun $MnO_x$ Fibers

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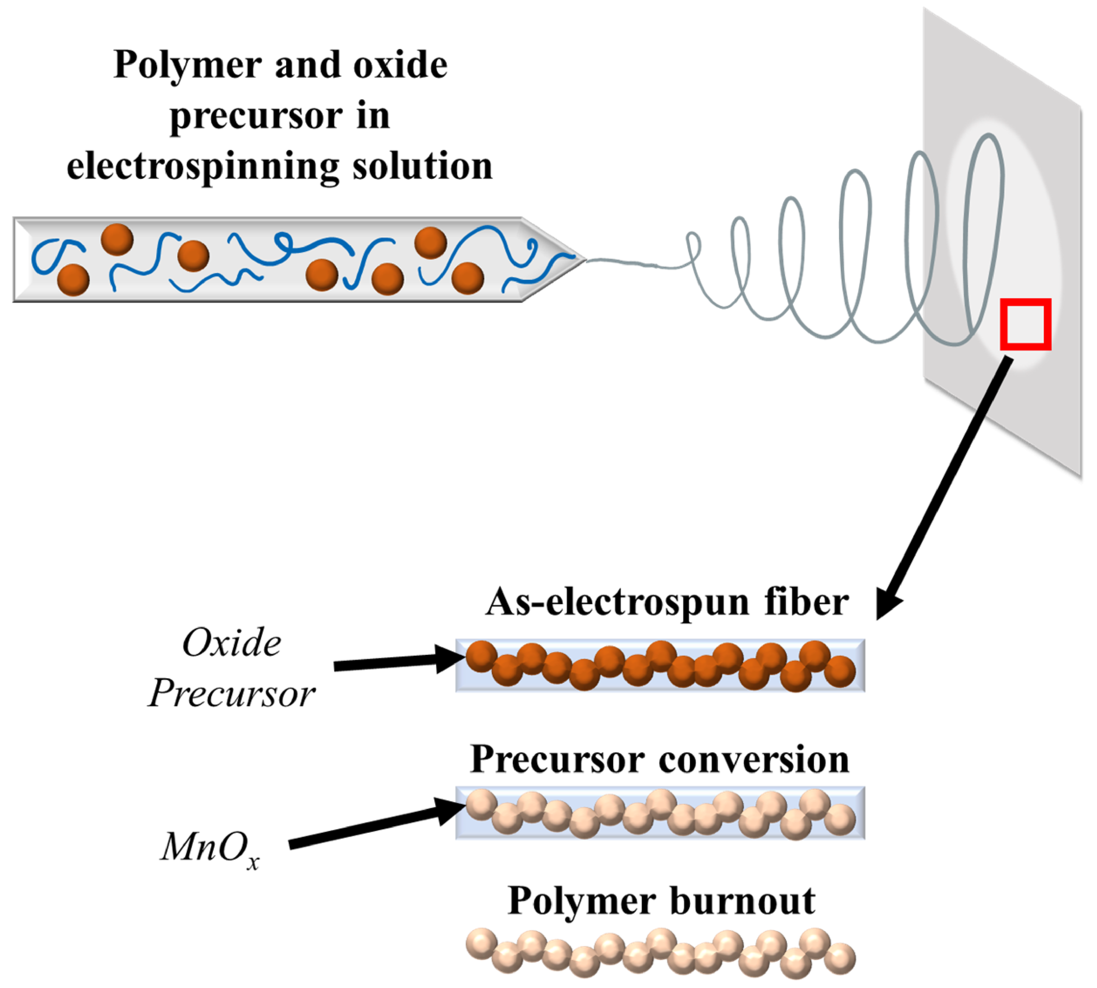
## Motivation

- Supercapacitors are a next-generation energy storage technology with high power and energy densities.[1]
- Nanostructured electrodes maximize surface area and theoretical capacity; manganese oxides are low-cost, low-toxicity electrode materials.[2]
- Electrospinning and thermal treatments are used to prepare nanofiber-based electrodes.
- Calcination conditions affect structure and composition of the ceramic fibers.[3]
- The effects of calcination pressure and time on fiber properties are studied herein.




## Materials and Methods

**Fiber Electrospinning and Calcination**

Fibers were electrospun from a solution of 8% *w/v* polyvinylpyrrolidone and 8% *w/v* manganese (II) acetate ($(CH_3COO)_2Mn$) in a solvent of 7:5:2 ethanol : acetic acid : deionized water by volume .

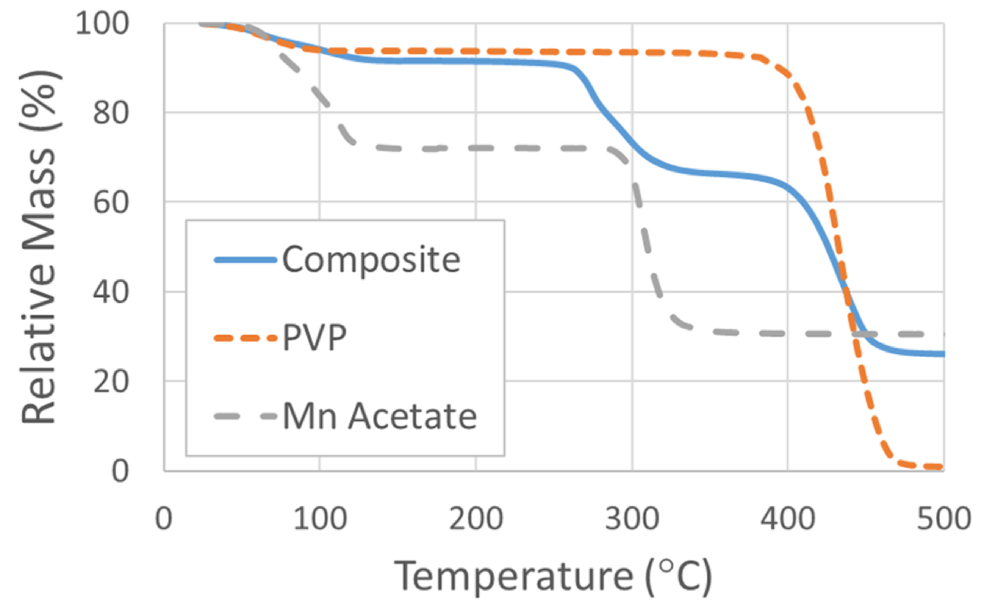
Fiber samples were heated to 600 °C and held at temperature for 30 min, 120 min, or 240 min before cooling to room temperature. Air pressure in the furnace tube was controlled to –0.070, -0.057, or 0.00 MPag (0.12, 0.26, or 0.81 atm) for the duration of the heat treatment.

**Cyclic Voltammetry (CV)**

Calcined samples were mixed with acetylene black and PVDF binder in a 70:15:15 weight ratio. The powders were mixed with N-methyl pyrrolidinone to form a thick slurry, which was doctor bladed onto Ni mesh substrates and dried.

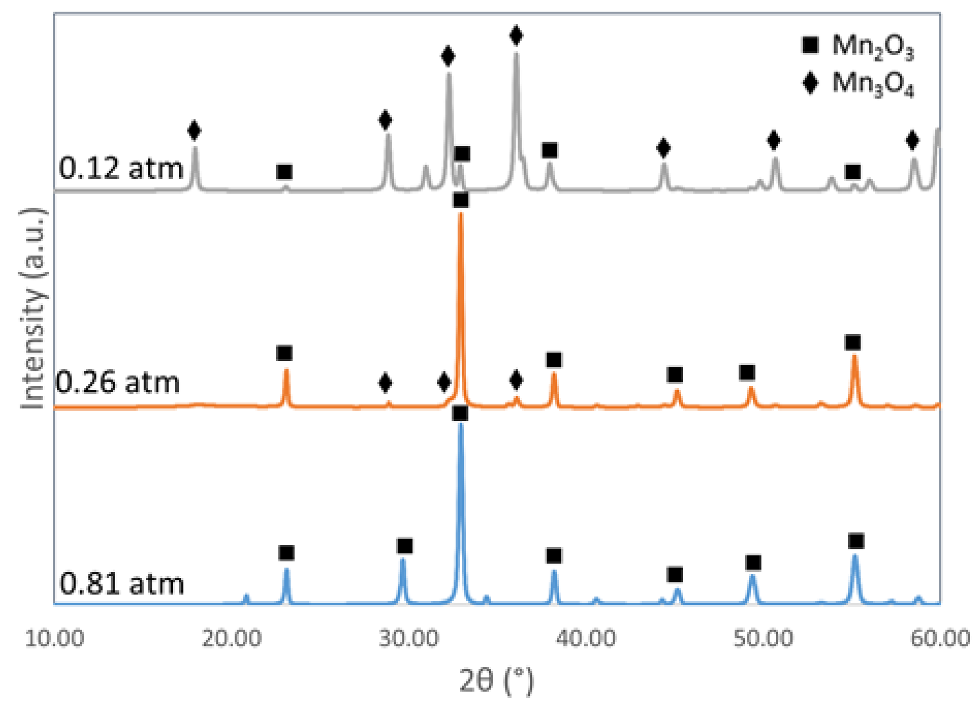
Electrochemical characterization was performed in 0.5 M $Na_2SO_4$ with a Pt wire counter electrode and Ag/AgCl reference electrode.

## Phase and Morphology

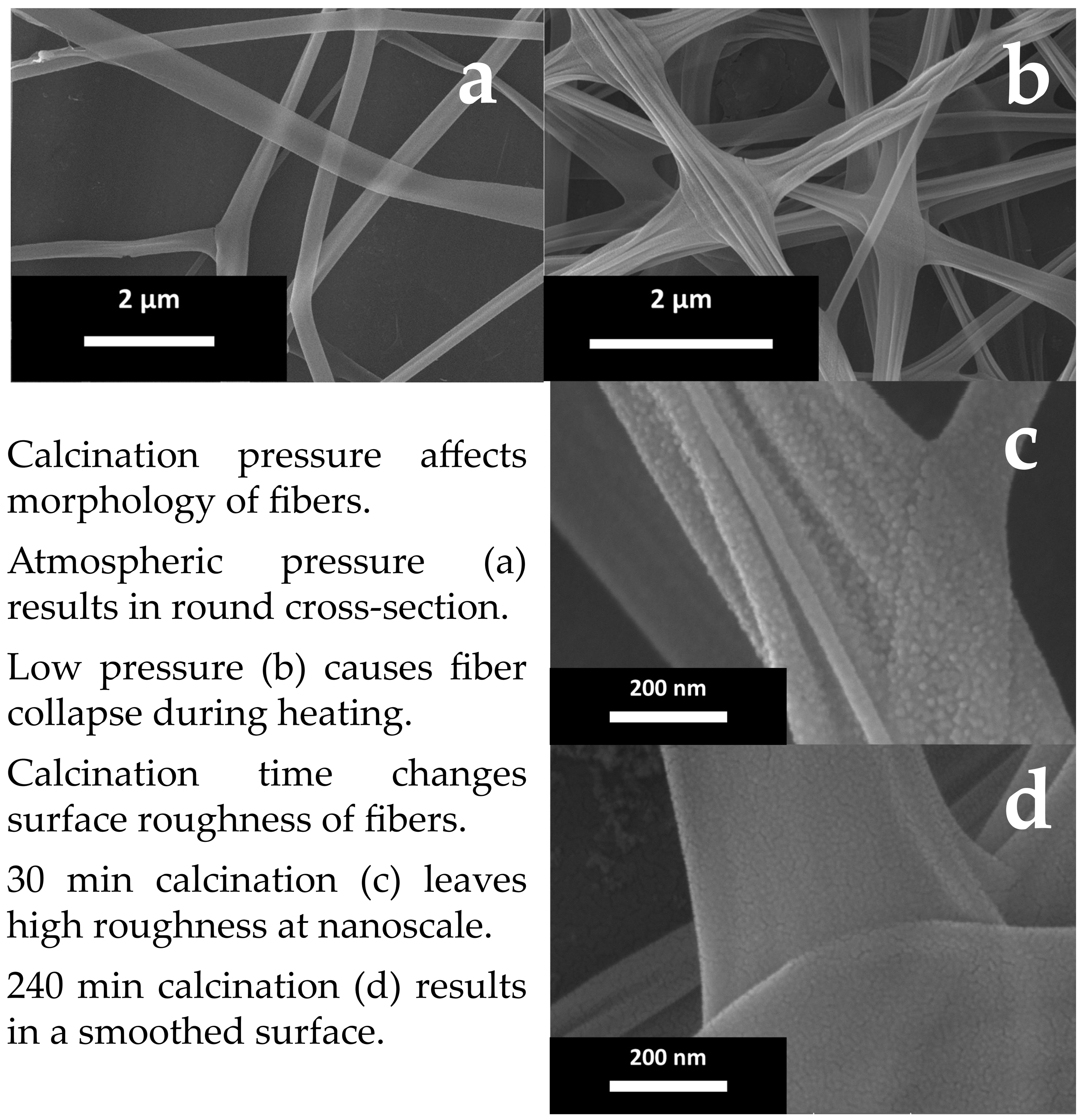



- Thermogravimetry is used to examine thermal behavior of the composite system.
- Conversion to ceramic occurs around 290 °C.
- Polymer is removed at 450 °C.

| Pressure (atm) | $Mn_2O_3$ (%) | $Mn_3O_4$ (%) |
|---|---|---|
| 0.12 | 4. | 96. |
| 0.26 | 70. | 30. |
| 0.81 | 100. | – |




- X-ray diffraction shows the relative phase composition of the calcined products.
- Calcination pressure affects phase distribution.
- At sub-atmospheric pressures, composition shifts from a higher oxidation state in $Mn_2O_3$ to the less-oxidized $Mn_3O_4$.



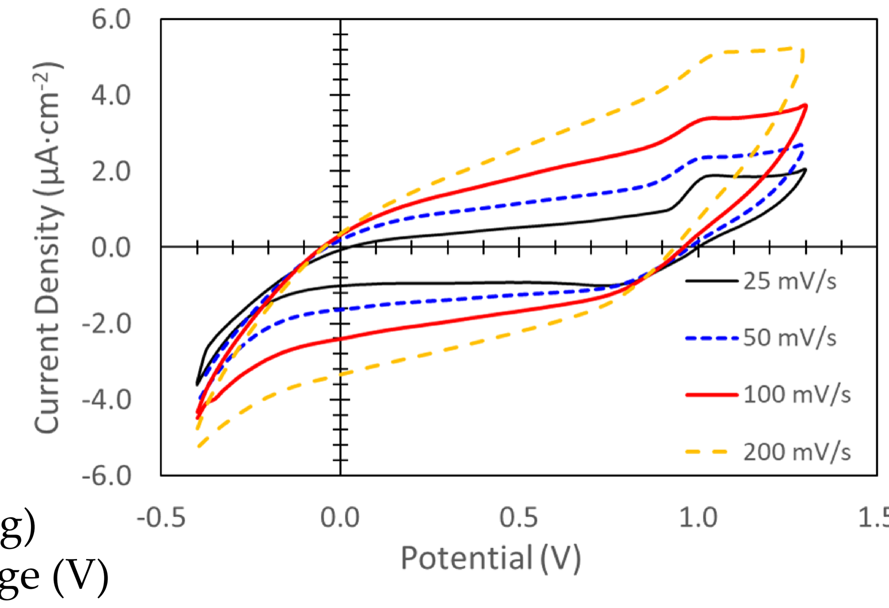

- Calcination pressure affects morphology of fibers.
- Atmospheric pressure (a) results in round cross-section.
- Low pressure (b) causes fiber collapse during heating.
- Calcination time changes surface roughness of fibers.
- 30 min calcination (c) leaves high roughness at nanoscale.
- 240 min calcination (d) results in a smoothed surface.

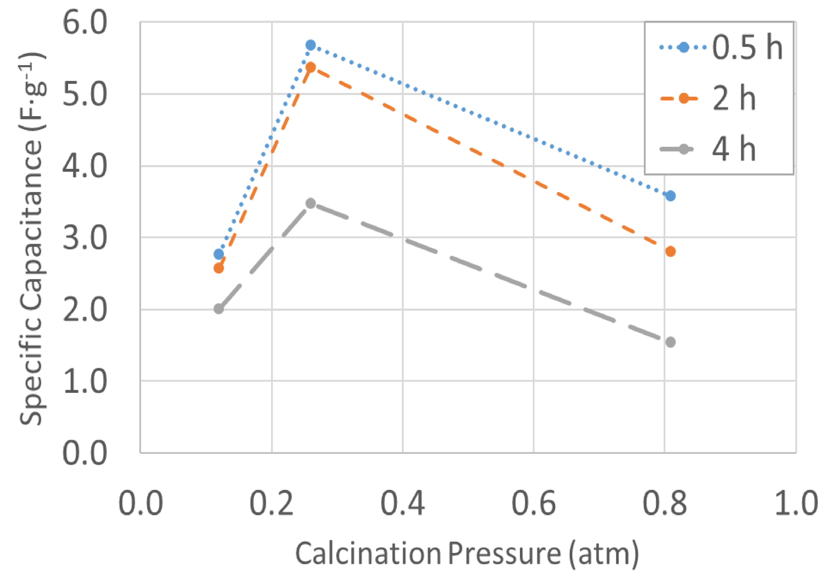
## Electrochemical Characterization

- Cyclic voltammetry is used to measure specific capacitance.
- Specific capacitance is calculated by:

$$C = \frac{\int i v dv}{\mu m \Delta V}$$

$i$ = current (A)
$v$ = voltage (V)
$\mu$ = scan rate (V/s)
$m$ = active mass (g)
$\Delta V$ = voltage range (V)




- Shorter calcination results in higher surface area and capacitance.
- Performance is elevated at mixed-phase composition due to enhanced charge transfer between phases.

## Conclusions

- Electrospinning and calcination may be used to fabricate manganese oxide fiber-based electrodes.
- Calcination pressure and time affect energy storage capacity through fiber composition and structure.
- Short calcination times cause nanoscale surface roughness with increased specific surface area and energy storage capacity.
- Moderate pressure results in mixed-phase $Mn_2O_3$ and $Mn_3O_4$ with elevated performance.

## References & Acknowlegements

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2)Arico, A., Bruce, P., Scrosati, B., Tarascon, J.-M., and Schalkwijk, W. *Nat. Mater.* **4**, pp. 366-377, 2005.
3)Lee, E., Lee, T., and Kim, B.-S. *J. Power Sources* **255**, pp. 335-340, 2014.
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## Student Profile

Molly is a Materials Science Ph.D. student from Anchorage, AK. Post-graduation she plans to move into industrial research. She holds a B.S. in Metallurgical and Materials Engineering from Montana Tech.