

# Lithium Silicide Encapsulated Porous Carbon Thin Films for Lithium Ion Batteries



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## I. Motivation

Improved energy storage is a critical component of reaching an energy-sustainable future. Lithium ion batteries are very promising due to their relatively high energy density, slow loss of charge when idle, and essentially no memory effect<sup>1</sup>. However, their charge capacity, cyclability, and energy and power densities need to be improved to meet our energy demands. In order to accomplish this goal, new electrode materials are being investigated. Silicon is promising in that it has a charge capacity six times higher than graphite, the currently used material; however, silicon has poor cyclability due to its extreme volumetric expansion during lithiation, which causes a loss of electrical contact and a cyclic gain and loss of a solid-electrolyte interface (SEI).

## II. Theory

Current techniques to accommodate for the expansion and contraction of silicon involve creating a carbon shell with a preset void space around a silicon particle. While this protects against damage to the carbon shell and an accumulating SEI layer, it does not provide a customized fit for each silicon particle; void spaces that are too large waste valuable volume, while void spaces that are too small risk cracking the carbon shell<sup>2</sup>. Our method (shown in Figure I) solves this problem by first delithiating  $\text{Li}_x\text{Si}$  to create void spaces in situ which will perfectly accommodate the volumetric expansion and contraction of each silicon particle, provided the same  $x\text{Li}$  is cycled each time. By starting with a polystyrene-based porous carbon thin film (PCTF), we are easily able to encapsulate the  $\text{Li}_x\text{Si}$  nanoparticles.

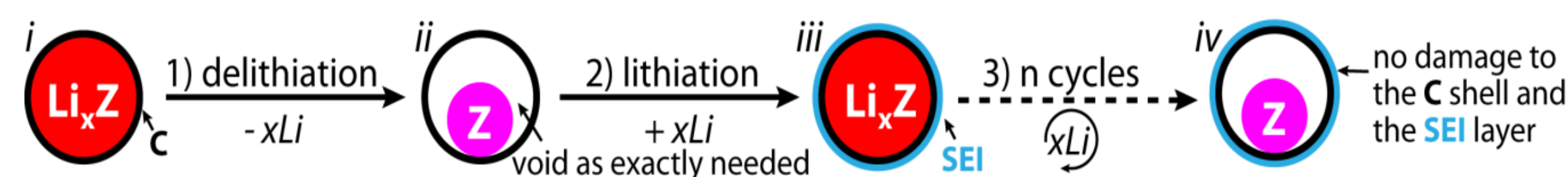


Figure I. Proposed method of starting with  $\text{Li}_x\text{Si}$  to create perfectly sized void spaces to accommodate the expansion and contraction of silicon without damaging the carbon shell or the SEI layer.

## III. Procedure

1. Synthesized  $\text{Li}_x\text{Si}$  using ball miller for 100 minutes.
2. Made polyacrylonitrile (PAN) solution in glovebox using dimethylformamide (DMF) as a solvent, stirred 1.5 hours.
3. Added  $\text{Li}_x\text{Si}$  and stirred 30 minutes.
4. Added pore source, stirred 30 minutes to 1 hour.
5. Drip coated slide, let dry under argon at room temperature for 18 hours, then let dry in air at 110 °C for 18 hours.
6. Carbonized in tube furnace under argon at 250°C for ½ hour and then at 600°C for 1 hour.
7. Characterized by Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD).

## IV. Results

### IVa. Porous Carbon Thin Films

PCTFs were fabricated using the procedure given in Section III, but no  $\text{Li}_x\text{Si}$  was added in making these samples. This was done to determine the ideal composition of porous carbon thin films without the influence of  $\text{Li}_x\text{Si}$ . The results of selected trials are shown in Figure II.

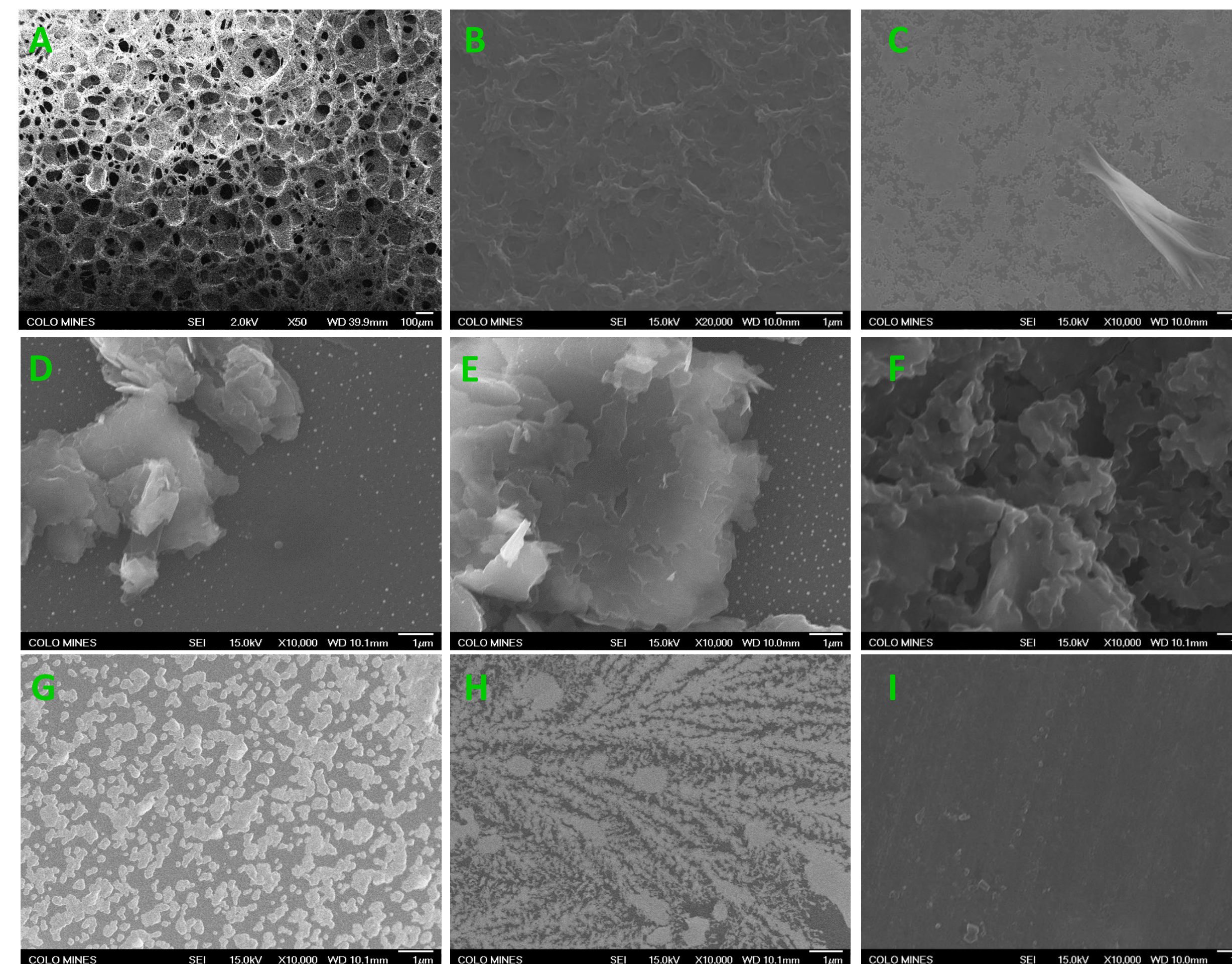


Figure II. SEM images of selected PCTFs of the following compositions:

- A: 15 wt.% PS, 7.5 wt.% dodecane in DMF
- B: 2 wt.% PAN, 1 wt.% oleylamine in DMF
- C: 2 wt.% PAN, 1 wt.% Styrene in DMF with  $\text{Al}_2\text{O}_3$
- D: 30 wt.% Polystyrene-block-polybutadiene-block-polystyrene in DMF
- E: 2 wt.% PAN + 1 wt.% Polystyrene in DMF
- F: 5:1 Polystyrene-co-Polyacrylonitrile PAN as 10 wt.% solids in DMF
- G: 2:1 PAN: Adiponitrile as 10 wt.% solids in DMF
- H: 2:1 PAN: Benzonitrile as 10 wt.% solids in DMF
- I: 2:1 PAN: Dodecanitrile as 10 wt.% solids in DMF

### IVb. $\text{Li}_x\text{Si}$ Embedded Nanoparticle Encapsulated Porous Carbon Thin Films

PCTFs were fabricated using the procedure given in Section III. The addition of  $\text{Li}_x\text{Si}$  had a positive effect on the quality and quantity of the pores created.

### IVb. Continued

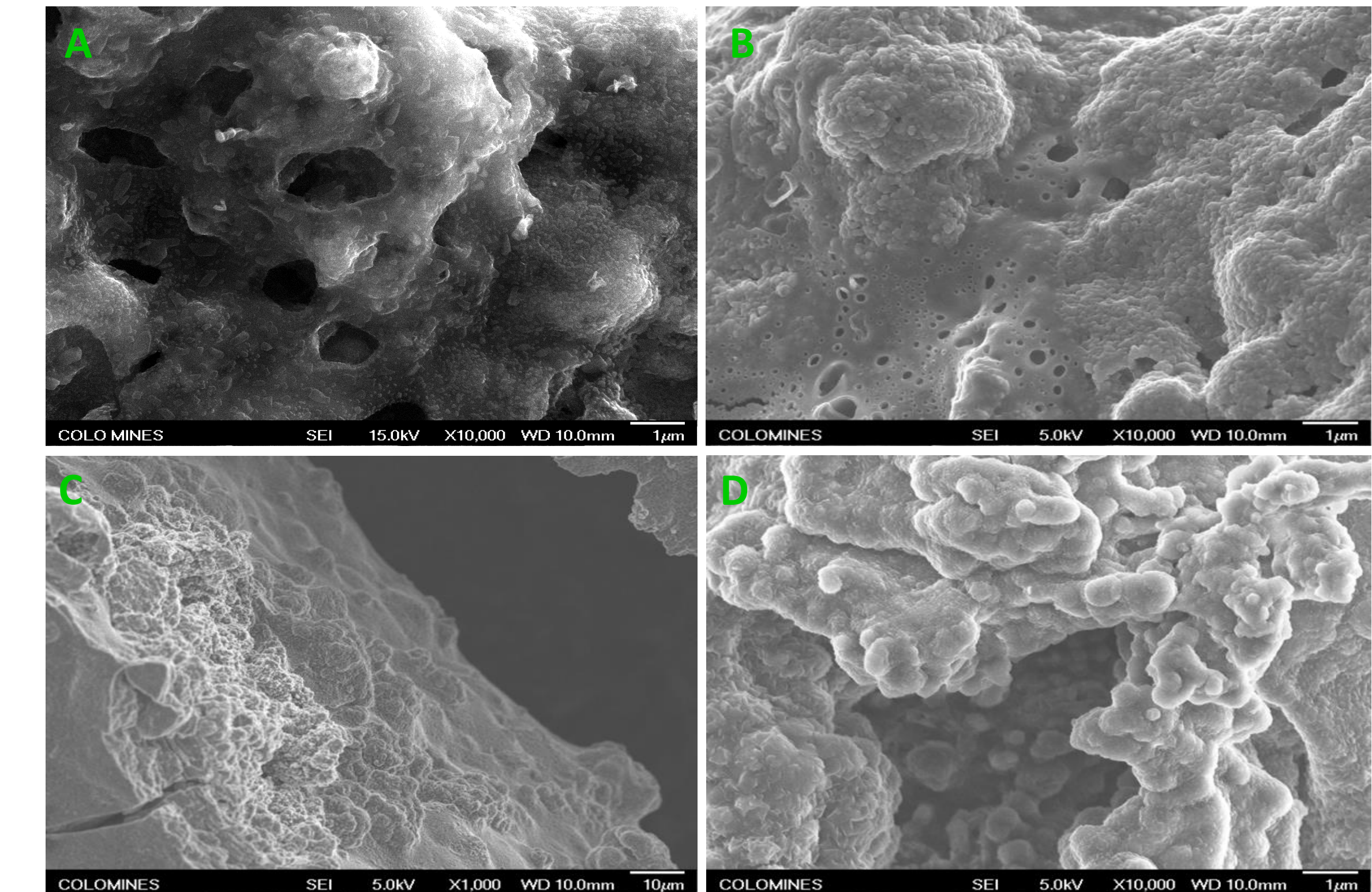


Figure III. SEM images of selected  $\text{Li}_x\text{Si}$  embedded nanoparticle porous carbon thin films of the following compositions:

- A: 95:5 wt. % PAN:PS-co-PAN porous thin film with  $\text{Li}_{4,4}\text{Si}$  nanoparticles embedded.
- B: 95:5 PAN:PS-co-PAN with 53 wt.%  $\text{Li}_{3,75}\text{Si}$  nanoparticles embedded.
- C: Cross-sectional view of 95:5 wt. % PAN:PS-co-PAN as 10 wt.% solids in DMF with 37 wt.%  $\text{Li}_{4,4}\text{Si}$  showing that the pores are throughout the sample.
- D: 95:5 wt. % PAN:PS as 10 wt. % solids in DMF with 42 wt.% embedded  $\text{Li}_{4,4}\text{Si}$  nanoparticles

## V. Conclusions and Future Work

We developed an effective method to fabricate PCTFs with and without embedded  $\text{Li}_x\text{Si}$  nanoparticles. The best PCTFs were generated using 95:5 wt.% PAN: pore former as 10 wt. % solids in DMF. Future work will take these results to make a lithium ion battery with a PCTF  $\text{Li}_x\text{Si}$  nanoparticle embedded anode material.

## VII. Acknowledgements

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## VIII. References

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- (2) Liu, N.; Wu, H.; McDowell, M. T.; Yao, Y.; Wang, C. M.; Cui, Y. "A Yolk-Shell Design for Stabilized and Scalable Li-Ion Battery Alloy Anodes", *Nano Letters* **2012**, *12*, 3315-3321.