

# Carbon-Coated $\text{Li}_7\text{Pr}_{2.5}\text{Nd}_{0.5}\text{W}_2\text{O}_{12}$ : Garnet as an Anode Material

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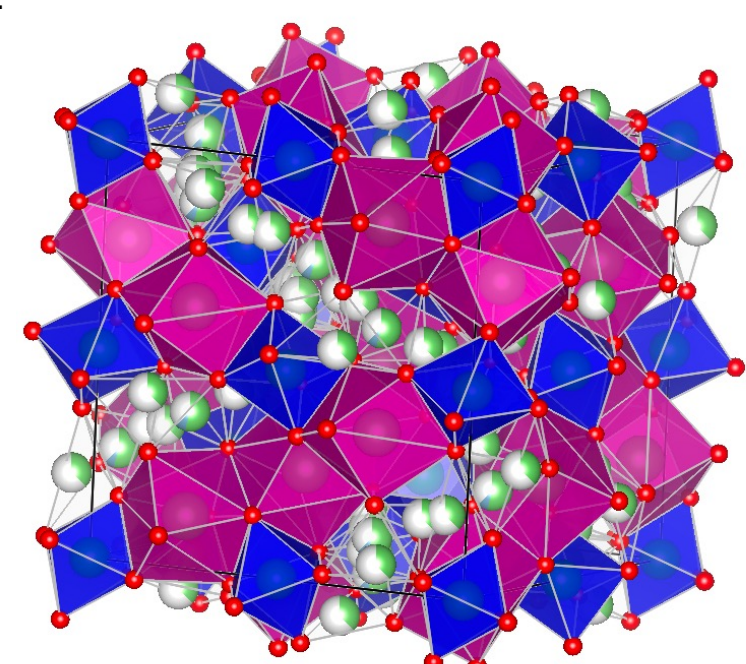
## Abstract

The aim of this work is to investigate the possibility of making porous material similar to the carbon-coated  $\text{Li}_7\text{Pr}_{2.5}\text{Nd}_{0.5}\text{W}_2\text{O}_{12}$  (C-LPNWO) for lithium-free batteries. By making a lithium garnet anode material with mixed ionic and electronic conductivity, we can test its performance relative to known anodes and determine its eligibility as a porous material. This porosity is necessary for the integration of the anode material into the Wachsman group's previously developed 3D architecture.<sup>1</sup> In this experiment, we found our hypothesis to be true – the electronic and ionic conductivity increases due to the carbon coating on the LPNWO grains in combination with the W reducing from a +6 to +4 oxidation state. These initial results are promising, and with further testing C-LPNWO may be a viable MIEC garnet material for Li-free batteries.

## Background

Lithium-stuffed garnet-type oxides have been extensively researched as a type of solid electrolyte material. However, Satish et al. first demonstrated its potential as an electrode, specifically as a low-voltage insertion anode that rivals graphitic anodes. They used a similar formula, carbon-coated  $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ .<sup>2</sup>

As an orthosilicate, the garnet structure follows the general formula  $\text{A}_3\text{B}_2(\text{SiO}_4)_3$ . In lithium garnet, the lithium replaces the silicon, lanthanides fill the A site, and transition metals occupy the B site. This structure leaves room for various combinations of lanthanides and transition metals with different ranges of oxidation states.



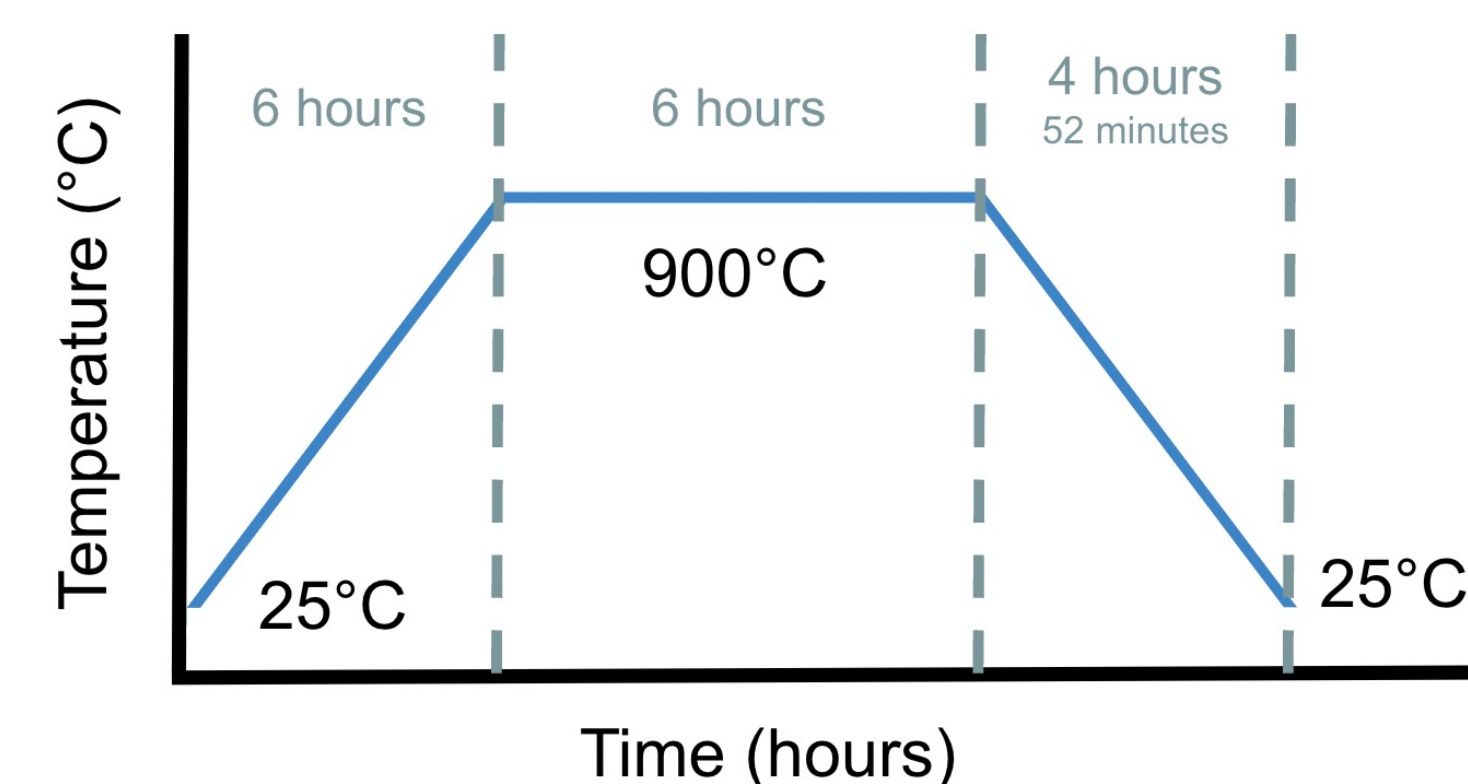
The unit cell of a typical garnet structure. The pink dodecahedra are A sites and the blue octahedra are B sites.

A major challenge with using garnet as an anode material is its lower electronic conductivity in comparison to existing anodes. By using both Praseodymium combined with Neodymium in the A site, the multivalence of the Praseodymium and Neodymium increases the electronic conductivity of the material.

Additionally, the Tungsten occupying the B site has a wide range of oxidation states, allowing it to reduce from +6 to +4. This increases the electronic conductivity compared to typical lithium garnets while allowing more lithium ions per mole of LPNWO.

## Milling, Calcination, Carbon-Coating

I first added the LPNWO's precursors in isopropanol to a milling bottle with 10mm milling media and let it mill for one day. I strained the slurry into a beaker and set the slurry to dry for one day in a 100°C drying oven. Once dry, I ground the resulting powder into fine grains and poured it into an MgO crucible before calcining the powder for 6 hours at 900°C.



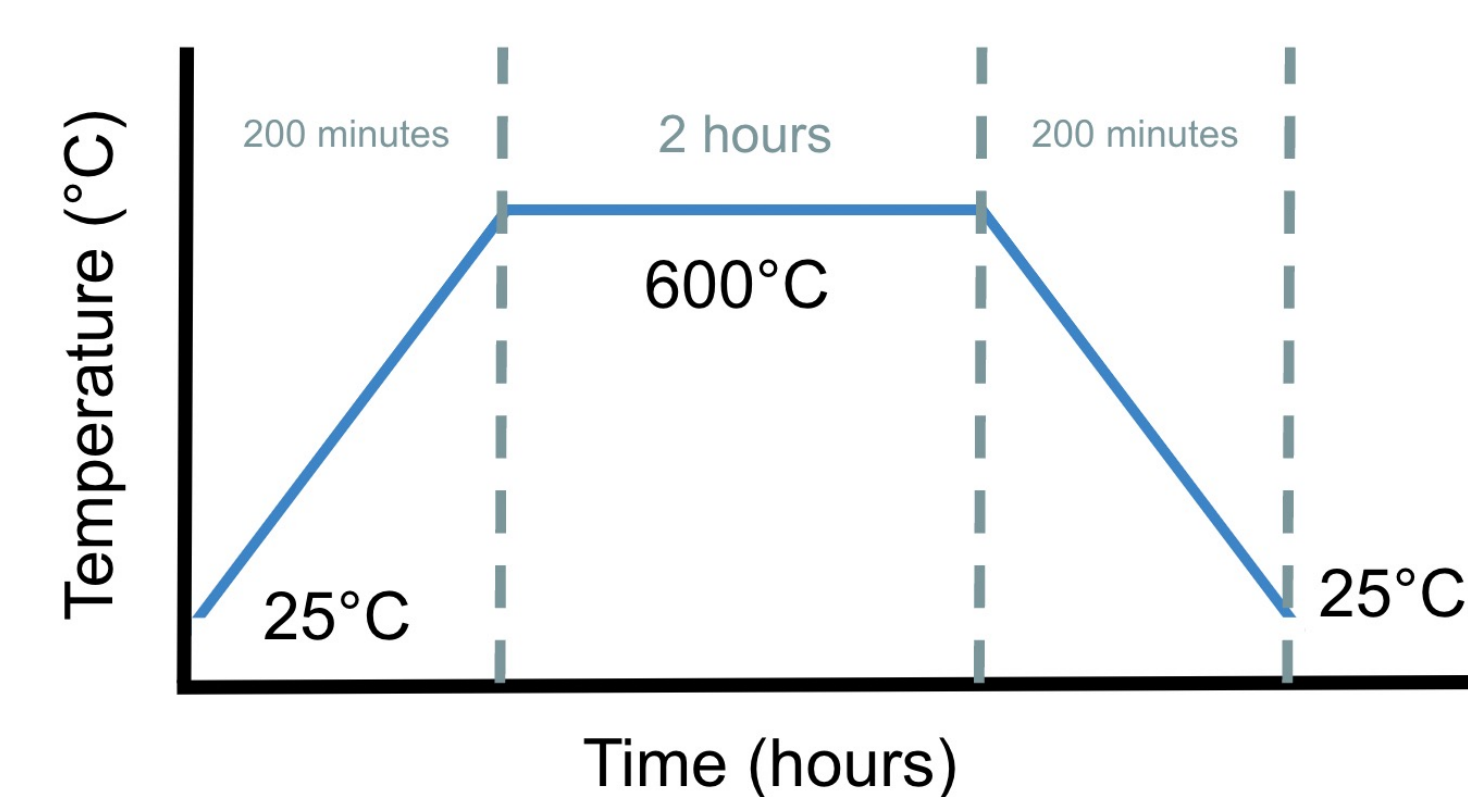
The temperature profile for the LPNWO calcination process. The powder was held at 25°C past the 4 hours and 52 minute mark since the process ran overnight.



I milled the calcined powder for one day in the same milling conditions as before and let the slurry dry in the drying oven until it was a powder. Half of the powder was then ready for tape casting while the other half was ready for carbon-coating.

About 15g of LPNWO powder remained after calcination. The powder's color matches the bright green of the W oxide precursor.

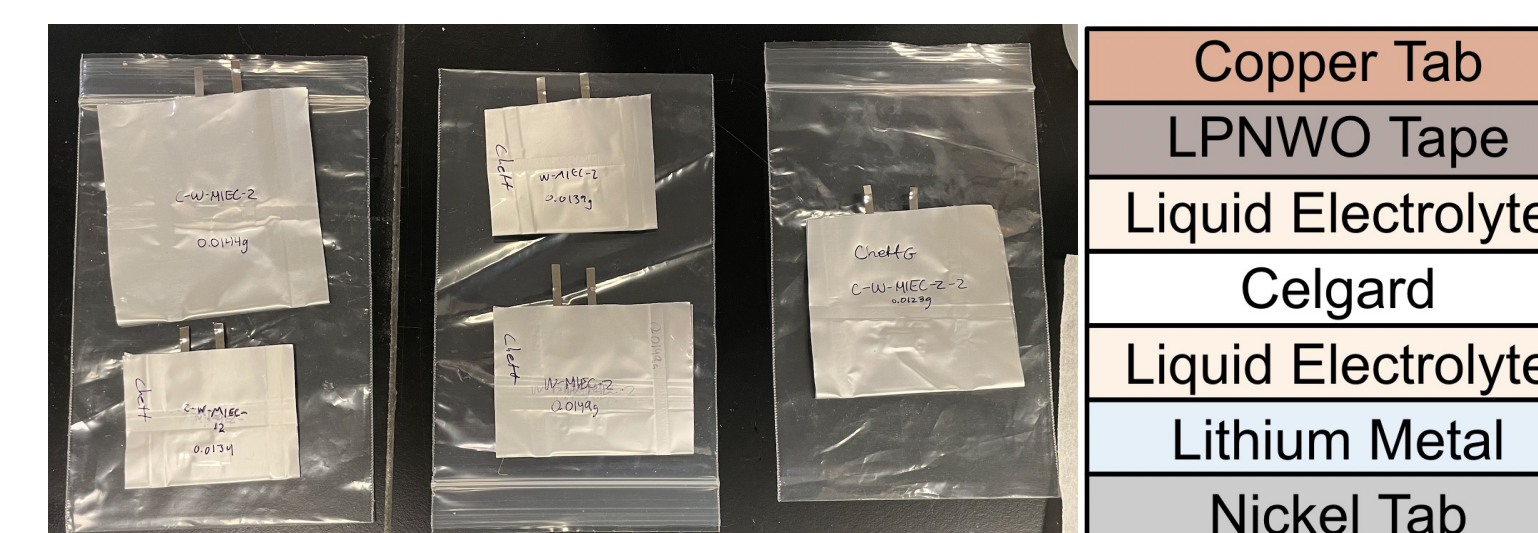
To carbon coat, I melted sucrose in a 3:1 ethanol to de-ionized water mix at 80°C while being stirred continuously for one hour. Then I added the LPNWO powder in a 20:1 ratio LPNWO to carbon and let it stir at 80°C for a day. I ground up the dried sucrose-LPNWO mix and sintered the powder in Argon at 600°C for 2 hours. The C-LPNWO mix was then ready for tape casting.



The temperature profile for sintering the sucrose-coated LPNWO powder in Argon.

## Tape Casting and Pouch Cells

I mixed an 8:1:1 ratio of the LPNWO powder to super p conductive carbon to polyvinylidene fluoride (PVDF). The PVDF was in a 20:1 ratio N-Methylpyrrolidone (NMP) to PVDF, and I added a few extra drops of NMP to the mixing cup. I then mixed the slurry for 1-2 minutes at 1800 rpm in a centrifugal mixer (1 minute for C-LPNWO, 2 minutes for LPNWO) and cast the slurry onto copper foil at a thickness of about 300µm.



The pouch cells and a diagram of their layers. The Celgard is a polypropylene separator and the liquid electrolyte is  $\text{LiPF}_6$ .

After letting the tapes dry at 120°C and pressing them to 2 tons, I cut them into 1x0.5cm tabs and scraped 1/3 of the tape off each tab to expose the Cu foil. I spot welded the tabs to nickel welding tabs and pressed lithium metal onto nickel tabs with nickel foil welded together. I then made two pouch cells to run cyclic voltammetry tests on.

## Results

We ran cyclic voltammetry tests on the carbon coated and non carbon coated LPNWO pouch cells to determine their reversibility and gauge the anode's electronic conductivities relative to one another.

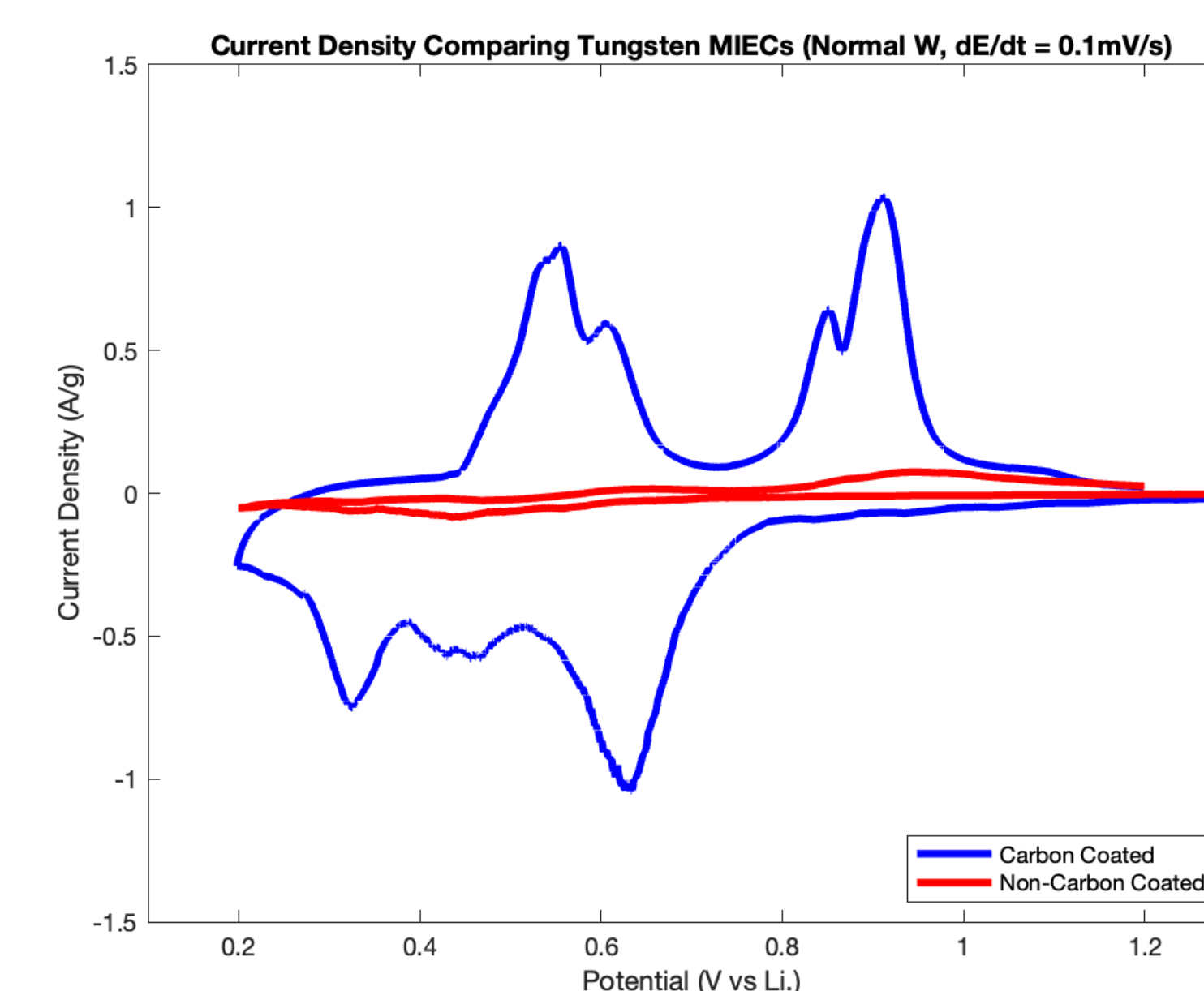


Figure 1: Comparing C-LPNWO with LPNWO relative to area of active anode material

## Analysis

Figure 1 compares the current density of the two cells scanned at a rate of 0.1mV/s between 0.2V and 1.2V. The two sharp peaks reflect the W reducing from +6 to +5 and once again from +5 to +4, matching our hypothesis. The carbon-coating significantly increases the electronic conductivity of the cell as seen by the wider range of the C-LPNWO curve. Additionally, the CV curve matches the results from Satish et al. with few discrepancies, indicating its reliability.<sup>2</sup>

We cycled the C-LPNWO cell twice at a scan rate of 0.1mV/s and found that the W reduction occurred at a lower potential during the second cycle. Further testing must be done to determine the source of this change.

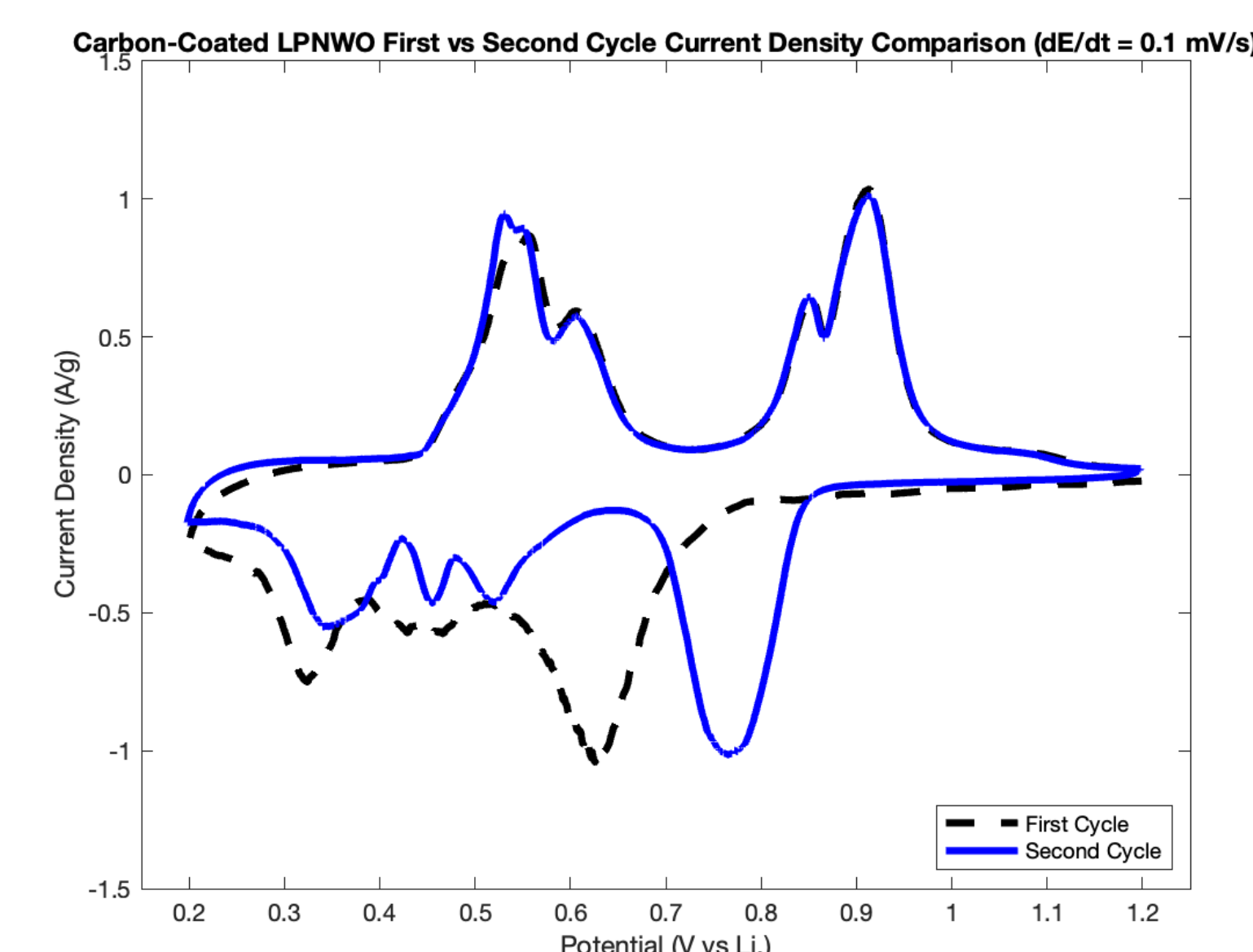


Figure 2: Comparing the current density change of the C-LPNWO cell between the first and second cycle at a 0.1mV/s scan rate

## Acknowledgements and References

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