

CLEAN RESOURCES FINAL REPORT PACKAGE

Project proponents are required to submit a Final Report Package, consisting of a Final Public Report and a Final Financial Report. These reports are to be provided under separate cover at the conclusion of projects for review and approval by Alberta Innovates (AI) Clean Resources Division. Proponents will use the two templates that follow to report key results and outcomes achieved during the project and financial details. The information requested in the templates should be considered the minimum necessary to meet AI reporting requirements; proponents are highly encouraged to include other information that may provide additional value, including more detailed appendices. Proponents must work with the AI Project Advisor during preparation of the Final Report Package to ensure submissions are of the highest possible quality and thus reduce the time and effort necessary to address issues that may emerge through the review and approval process.

Final Public Report

The Final Public Report shall outline what the project achieved and provide conclusions and recommendations for further research inquiry or technology development, together with an overview of the performance of the project in terms of process, output, outcomes and impact measures. The report must delineate all project knowledge and/or technology developed and must be in sufficient detail to permit readers to use or adapt the results for research and analysis purposes and to understand how conclusions were arrived at. It is incumbent upon the proponent to ensure that the Final Public Report **is free of any confidential information or intellectual property requiring protection**. The Final Public Report will be released by Alberta Innovates after the confidentiality period has expired as described in the Investment Agreement.

Final Financial Report

The Final Financial Report shall provide complete and accurate accounting of all project expenditures and contributions over the life of the project pertaining to Alberta Innovates, the proponent, and any project partners. The Final Financial Report will not be publicly released.

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CLEAN RESOURCES FINAL PUBLIC REPORT TEMPLATE

1. PROJECT INFORMATION:

Project Title:	Modified redox flow battery membranes for a step change improvement in energy storage technology
Alberta Innovates Project Number:	202101720
Submission Date:	
Total Project Cost:	
Alberta Innovates Funding:	
AI Project Advisor:	Susan Carlisle

2. APPLICANT INFORMATION:

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3. PROJECT PARTNERS

Please provide an acknowledgement statement for project partners, if appropriate.

RESPOND BELOW

The University of Waterloo prepared graphene coated membranes for laboratory scale battery testing at the University of Calgary. They also developed and evaluated roll-to-roll coating process for scale up of the technology.

Evercloak provided in-kind support including advice on the scale-up of the coating process, attending project meetings, reviewing and giving feedback on progress reports and research results. In addition, they provided access to their facilities for preliminary testing the scale up of the coating process.

StorEn provided in-kind support including advice on the implementation of the coated membrane in a commercial vanadium redox flow battery, attended meetings to discuss the progress of the research, and gave feedback on the research results and the commercial potential of the technology.

A. EXECUTIVE SUMMARY

Provide a high-level description of the project, including the objective, key results, learnings, outcomes and benefits.

RESPOND BELOW

Low carbon electricity grids require cost effective, flexible energy storage technologies to enable intermittent renewable sources, such as wind and solar, to be dispatched whenever electricity is needed. Redox flow batteries (RFBs), which store energy in liquids, are a leading candidate for utility-scale electricity storage applications as they have a long life and flexible design. Although the cost of RFBs are reducing as the technology matures, there is a need for significant reductions in cost to enable widespread implementation. In this project, a novel membrane technology was developed and evaluated for RFBs. The membrane technology involves modifying the commercial membranes that are currently used with a single layer of an emerging nanomaterial developed in the laboratory at the university of Calgary: electrochemically exfoliated graphene). The production of the nanomaterial and the membrane coating process use low-cost materials and simple, scalable processes. Preliminary laboratory testing indicated that the membrane could significantly enhance the power output of vanadium RFBs (VRFBs), the most commercially advanced of RFB technologies. An increase in power density will reduce the cost of this battery technology, enhancing its viability for energy storage applications including renewable integration and electricity grid stabilization. In addition, the membrane can improve the cycling stability, reducing the maintenance and operating costs of commercial installations.

During the project, it was determined that the increase in power density was dependent on the electrode material used in the battery. The membrane modification process was optimized to achieve an increase

in the VRFB power density of more than 50%, one of the original targets for the project. This enhancement was obtained with a laboratory VRFB using carbon paper electrode, commonly used in research laboratories. However, laboratory testing performed by a VRFB industry collaborator was not able to reproduce the enhanced power density. It was determined that with the felt electrodes normally used in commercial VRFB, the power density was not enhanced by the use of the modified membrane. However, the improved cycle stability can be an important benefit of the membrane modification, and further laboratory studies are needed to optimize the membrane for cycle stability rather than power density.

The project has provided new insights into the role of membranes in VRFB, and provided a pathway for further development of modified membranes for RFB applications. Further laboratory scale development is needed to optimize the membrane coating process for enhanced cyclability for VRFB and other RFB chemistries. In addition, techno-economic analysis is needed to evaluate the benefits of the membrane coating in the commercial context of energy storage using RFBs. Although an increase in power density in commercial RFBs was not achieved during the project, it is likely that this will be possible using the technology developed in the project. Increasing cycle stability of commercial membranes will allow the use of thinner, lower resistance membranes, which will reduce losses and increase VRFB power density. The emergence of the membrane coating process developed in this project provides a new innovative approach for RFB developers to exploit in order to reduce the cost of RFBs for energy storage applications. Reduce the cost of RFBs for energy storage applications will be critical to unlock and accelerate the implementation of renewable energy and stabilize electricity grids across the globe. However, further development work is needed in order to achieve this goal.

B. INTRODUCTION

Please provide a narrative introducing the project using the following sub-headings.

- **Sector introduction:** Include a high-level discussion of the sector or area that the project contributes to and provide any relevant background information or context for the project.
- **Knowledge or Technology Gaps:** Explain the knowledge or technology gap that is being addressed along with the context and scope of the technical problem.

RESPOND BELOW

Battery technologies are attractive for utility-scale electricity storage since they are flexible and provide fast response, ensuring reliable electricity supply. The membrane technology will be targeted for use in vanadium RFBs (VRFBs) for use in stationary electricity storage applications including residential, commercial and utility sectors. The membrane technology can be fitted directly into existing commercial RFBs or used in RFB technologies under development.

With increasing implementation of cheap renewable energy generation, there is an increasing need for versatile battery energy storage technologies to increase the reliability and quality of electrical energy supplies. The size of energy storage systems includes both the power that can be delivered when the

stored energy is discharged (MW), and the total amount of energy that can be stored (MWh). The latter can also be specified as the duration that the power can be provided during discharge (hours). Unlike conventional battery technologies, such as lithium-ion, redox flow batteries (RFBs) store energy in liquid electrolytes that are pumped through the battery (see project image), so that the power and energy storage capacity can be independently specified, by varying the amount of liquid electrolyte used. Compared to the widely used lithium-ion batteries, RFBs offer other advantages for these applications, including very long cycle life, low life-cycle cost, and ease of recyclability. As RFB technology matures, they are expected to take an increasing share of the growing energy storage market. The disadvantages of RFBs include their relatively low energy density, and for the most developed RFB technology, the price volatility of the vanadium electrolyte used. RFBs not only provide benefits through energy storage, but as they can respond rapidly, they can provide ancillary services such as frequency and voltage control for electricity networks. Battery storage will be increasingly integrated with large generating facilities or distribution networks, at the point of use in microgrids, or behind the meter to support distributed generation (e.g. residential solar power) and manage demand. However, there remains a need to reduce the cost and increase the performance of battery technologies, to achieve an attractive economic return for their implementation in the majority of electricity supply applications.

RFBs use two tanks of liquid electrolytes that are circulated through the battery (see project image above), to provide the positive and negative voltage of the battery output. Inside the battery, the electrolytes must be separated by a membrane that allows the passage of ions, but minimizes the crossover of the active species (e.g. vanadium). The membrane has a significant impact on both the performance and cost of the battery, accounting for 30-40% of the stack costs and 10-20% of system cost. Improvements in the membrane directly impacts the performance of the battery, in particular its efficiency, energy and power density. Improving these characteristics through membrane development will enable the capital and operating cost of RFB systems to be reduced, providing a significant economic driver. As the use of intermittent renewable generation increases, achieving cost-effective energy storage technology, targeted by the membrane development in this project, will drive lower prices for end-users, and reduce the environmental impact of electricity systems.

Most commercial RFBs use available ion-exchange membrane materials such as Nafion, which offer reliable performance and long-life. Researchers are currently developing new or modified membranes. However, these developments either have significant limitations, such as limited life, or present other challenges such as complex or costly manufacturing. Improvement in membrane properties often present a trade-off between the electrical resistance and the cross-over of active species. For example, the use of a composite membrane to reduce cross-over typically leads to higher resistance and thus lower battery efficiency, while reducing membrane thickness reduces the resistance but increases crossover. There is a crucial need for novel approaches that can both increase conductivity and reduce crossover. This would enable the use of a thinner membrane, offering a combination of lower cost, increased efficiency, and a smaller battery for a given power output (MW) and storage capacity (MWh).

C. PROJECT DESCRIPTION

Please provide a narrative describing the project using the following sub-headings.

- **Knowledge or Technology Description:** Include a discussion of the project objectives.
- **Updates to Project Objectives:** Describe any changes that have occurred compared to the original objectives of the project.
- **Performance Metrics:** Discuss the project specific metrics that will be used to measure the success of the project.

RESPOND BELOW

Electrochemical batteries convert electrical energy to chemical energy during charging, and vice-versa during discharging. The inter conversion occurs by electrochemical reactions that take place at the interface between two electrodes (an electrical conductor), and associated electrolytes (ionic conductors). For a VRFB, the electrodes are typically graphite felt, and the electrolytes are aqueous solutions of sulfuric acid and different vanadium species. The two sides of the battery are at different electrical potentials (voltages), and as mentioned above, the two electrolytes are separated by a membrane as shown in project image. Key performance characteristics of batteries include:

- Energy density – the ratio of the amount of energy to the mass or volume of the battery (Wh/kg or Wh/L).
- Power density – the ratio of the amount of power output to the projected area of the battery electrodes (W/sq. m). The power density can be calculated by multiplying the cell voltage and the current density (A/sq. m), which is the ratio of the electrical current flowing to the projected area of the electrodes.
- Energy efficiency – the ratio of the amount of energy recovered when the battery is discharged to the amount of energy used to charge the battery (%).

If the battery is charged and discharged at a constant electrical current, the battery efficiency can also be broken down into two components:

- Coulombic efficiency – the ratio of the electrical charge recovered during discharge to the charge supplied during charging (%).
- Voltage efficiency – the ratio of the average battery voltage during charging and the average voltage during discharge (%).

As discussed above, the membrane plays an important role in separating the active vanadium species on each side of the battery, and any cross-over of charged vanadium species will lead to a reduction in the coulombic and energy efficiency. In addition, during charging and discharging the current must flow through the battery membrane, and its resistance to current flow reduces the battery voltage and hence the power and energy density. To scale up the battery, a number of cells, each comprising the two electrodes, the membrane and electrolyte flow channels, are arranged in stacks of up to 100 cells. As

mentioned above, the ion-exchange membrane material is also a high cost item, contributing around 30-40% of the cost of the battery stack.

We have developed a novel membrane coating technology that enhances RFB performance without requiring modification to the battery design or operating conditions. Commercially available membrane materials that are currently being used in RFBs are modified by coating them with a single layer of graphene, a one atom thick carbon material with unique properties. Since RFBs currently use these membrane materials along with carbon or graphite electrodes, the modified membrane is fully compatible with current commercial RFB technology. The modified membrane can be incorporated directly in existing battery designs with no requirement for modification in fabrication or assembly of the battery. The technology integrates two recently developed processes:

- An innovative, low-cost graphene exfoliation process developed at the University of Calgary (UCalgary), through an Alberta Innovates Strategic Project. The process produces a high-quality exfoliated graphene, with >70% single and bilayer graphene flakes, high electrical conductivity and electrochemical activity.
- Membrane coating with a single layer of exfoliated graphene developed by our partners at the University of Waterloo. Coating is achieved by floating the graphene at an air water interface, and drawing the membrane through the interface. The process can be controlled to give a high coverage (>80%) of graphene flakes.

Coating a mono-layer of graphene on the RFB membrane leads to a step change in the performance of a VRFB, the most well developed and commercially available RFB energy storage technology. In laboratory tests, the round-trip efficiency, energy capacity and power output of the VRFB increased significantly. The increased energy capacity and power output enable an increase in the energy density and power density of a given battery design, and these are key performance metrics for battery technology.

The original objectives of the project were to:

1. Optimize the modified membrane technology using lab scale testing to enhance the performance of VRFBs.
2. Evaluate the impact of the novel membrane on the performance of lower cost, non-vanadium RFB technologies.
3. Integrate the membrane technology into a commercial VRFB.
4. Scale-up the technology to demonstrate the performance enhancement in a 5 kW, small commercial scale VRFB.
5. Achieve an increase in the power and energy density of the small commercial VRFBs of more than 50%.

The membrane technology was optimized to achieve ca. 50% increase in power density in our laboratory setup. However, during the project, it was discovered that the increased power density observed in preliminary laboratory experiments was not obtained when the battery design was modified to use similar materials to those used in industry. It was concluded that while the membrane offered some benefits for

battery operation, an increase in power density would not be achieved in a commercial scale battery. Consequently, it was determined that integration and scale up of the technology in to a commercial scale battery was not justified, and we did not pursue objectives 3 and 4.

D. METHODOLOGY

Please provide a narrative describing the methodology and facilities that were used to execute and complete the project. Use subheadings as appropriate.

RESPOND BELOW

The project focused on four key tasks:

1. Optimization of the graphene coated membrane.

The preparation of the membrane involved two steps: preparation of graphene powder, coating of a single layer of graphene particles on to a commercial battery membrane material. Graphene is a one atom thick layer of carbon, and is an emerging nanomaterial with unique properties. However methods for synthesis of graphene are typically difficult to scale up, high-cost, or produce a low quality product unsuitable for many applications. At the University of Calgary we have developed an innovative scalable electrochemical method for the synthesis of high quality graphene from a graphite starting material. The method operates at ambient conditions, uses cheap and non-toxic chemicals, and has low energy consumption, enabling low cost production of high quality graphene powder. During the project this process was optimized in the University of Calgary's labs for this application, and scaled up to kilogram scale. We found that the coverage of graphene was only a few mg per square meter, and kilogram scale production is thus sufficient for commercial application.

The graphene product was shipped to the University of Waterloo, where coated membranes were prepared. The coating method involves immersing the commercial membrane in a bath of a suitable liquid, floating the graphene powder on the liquid surface, and draining the liquid so that a single layer of graphene particles are deposited on the membrane. By careful control of the operating conditions a dense, uniform coating on the membrane can be achieved. The method could be repeated to obtain multiple layer coatings, or to coat both sides of the membrane.

After coating membrane samples were returned to the University of Calgary for testing. Membranes were tested in VRFB test stations to determine the impact of the membrane coating on battery performance. The coatings were optimized by varying the graphene synthesis conditions and the coating process.

2. Evaluation of other redox flow battery chemistries.

In addition to evaluation of coated membranes for the VRFB, membranes were also tested in alternative chemistries including a zinc-iodide flow battery and an all iron system. These emerging chemistries offer significant advantages over vanadium, such as high energy density (in the case of zinc iodide), and lower

cost. However, they also suffer from limitations that constrain their commercialization, in particular they often have poor cycling stability in comparison to vanadium. The impact of the membrane coating on the power density and cycling stability was evaluated using flow battery test stations suitable for these emerging chemistries at the University of Calgary.

3. Scale-up of graphene production from gram to kilogram scale

An electrochemical reactor suitable for production of up to 2 kg per day of graphene was designed and fabricated at the University of Calgary. The reactor was commissioned and tested under a range of operating conditions. The energy consumption and product yield were determined, and samples of graphene product were analyzed to determine the impact of scale up on the product quality.

4. Evaluation of Modified Membranes in a 5 kW Commercial Redox Flow Battery

Scale-up of the coating technology was achieved at the University of Waterloo using a roll-to-roll concept, where the membrane was drawn through the liquid surface and graphene was continuously added. A 5kW commercial VRFB was obtained from project partner StorEn. The battery was installed in a research microgrid facility at the University of Calgary. Preliminary charging and discharging of the battery was planned to obtain baseline data. It was planned to prepare battery stacks utilizing coated and uncoated membranes in order to evaluate the impact of the graphene coating on the battery performance. However, as discussed above, this part of the project was not pursued.

E. PROJECT RESULTS

Please provide a narrative describing the key results using the project's milestones as sub-headings.

- Describe the importance of the key results.
- Include a discussion of the project specific metrics and variances between expected and actual performance.

RESPOND BELOW

1. Optimization of graphene coating technology for VRFB

1.1 *Recommended electrolyte composition and operating conditions for graphene exfoliation process.*

The selection of the electrolyte composition affects the properties of the graphene. Experiments were performed to optimize the electrolyte during exfoliation. In addition, a comparison was carried out between the effects of graphene prepared in different electrolyte compositions on the reaction kinetics within the positive electrolyte of a VRFB. Electrochemical experiments were performed to study the impact of the exfoliation conditions on the vanadium electrochemistry. Based on these experiments, and battery performance experiments, the optimum conditions for synthesis of the graphene was identified. The characteristics of the graphene produced was evaluated by a wide range of techniques, including scanning electron microscopy, Raman and UV-Vis spectroscopy, surface area analysis, contact angle and

conductivity measurements. A wide range of operating conditions can be used for the graphene exfoliation. A detailed investigation of the impact of electrolyte composition and temperature on graphene characteristics was carried out. For example, Figure 1. shows some results on the effect of the electrolyte composition on the graphene conductivity, while Figure 2 shows the effect of exfoliation temperature. These investigations led to new insights into the impact of exfoliation conditions on the graphene characteristics. Based on these studies, a limited set of exfoliation conditions were selected for preparation of graphene for membrane coating and battery testing.

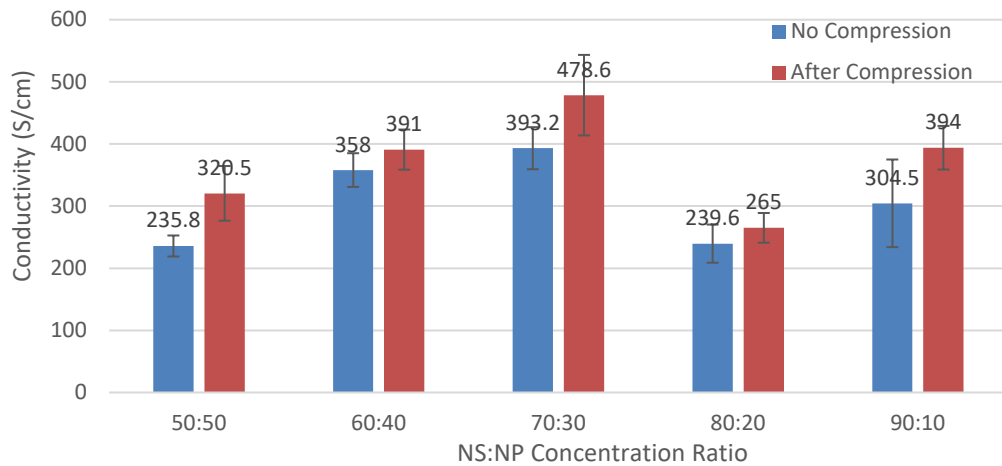


Figure 1. Electrical conductivity of graphene films exfoliated at using different electrolyte compositions.

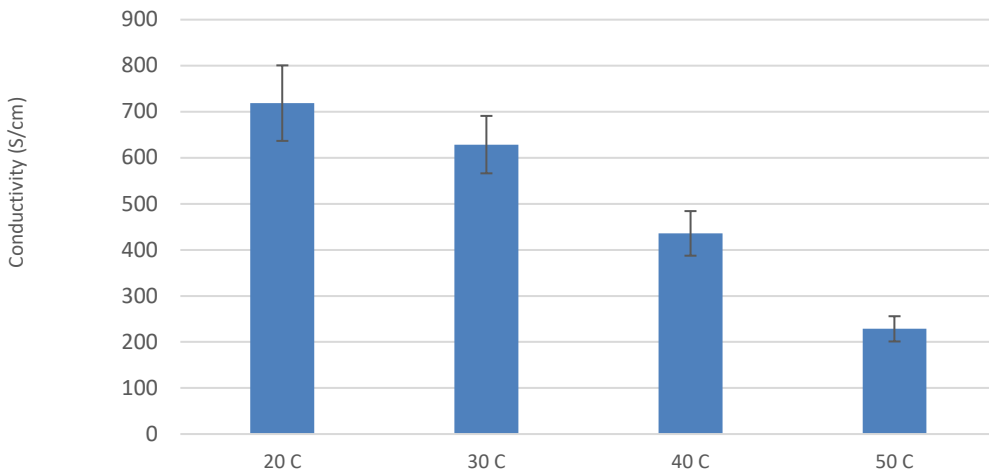


Figure 2. Conductivity of graphene films exfoliated at a range of temperatures.

1.2 Recommended coating conditions, number of layers and coating on one or both sides of the membrane.

Coating conditions, including equipment setup procedures and deposition fluid compositions, were optimized to produce consistent, high-quality coatings. The deposition fluid composition was improved and optimized to enhance the quality of the graphene coating. Methods were developed to enable reproducible characterization of the coated membrane. To characterize the graphene coating, a mica substrate was used to provide a flat surface enabling determination of the thickness distribution of the graphene by atomic force microscopy (AFM). An AFM image of a graphene coating is shown in Figure 3(left), which can be used to determine the layer number distribution from the height data as shown in Figure 3(right).

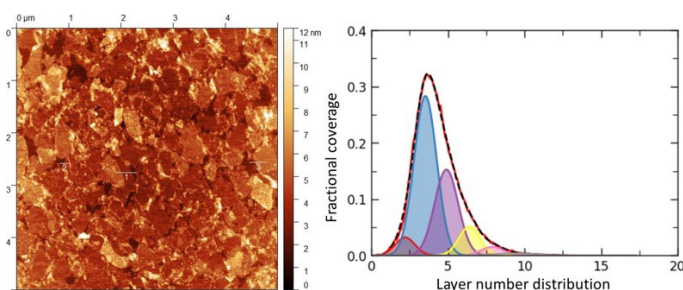


Figure 3: (Left) Atomic force microscopy images of a graphene coating to determine sheet average layer number and; (Right) Layer number distribution on coated Nafion membrane. The average film thickness was found to be 2.3-2.5 nm.

Coating conditions, including equipment setup procedures and deposition fluid compositions, were optimized to produce consistent, high-quality coatings. A range of different methods were used to characterize the coatings. Figure 4 and 5 show examples AFM and scanning electron microscopy (SEM) images of the bare Nafion and graphene coated Nafion membrane. From the SEM images (Figure 5 a and d), the change in the morphology of the top surface of the Nafion due to the graphene coating is clearly evident. The SEM and AFM images confirm that the graphene nano flakes (GNFs) are well-distributed over the Nafion surface. SEM images of membrane cross-section are shown in Figure 5. The AFM surface micrographs show a clear difference between bare Nafion (Figure 4a) and graphene coated Nafion (Figure 4b). Additionally, the graphene flakes appear wrinkled on the graphene coated membrane when compared to a coating of the same graphene dispersion on a flat mica substrate (Figure 4c). The graphene flakes wrinkle as the membrane shrinks rather than detaching from the membrane or sliding. The wrinkling is evidence that the strength of the interaction between the Nafion 117 and GNFs is enough to overcome the stiffness of the flakes.

The AFM images are consistent with SEM results for graphene coated membrane in Figure 5d and f. To confirm the presence of graphene on the membrane surface Raman spectroscopy was used. Figure 4d shows Raman spectra captured on the graphene coated side and the uncoated side of the Nafion 117 membrane. Well-defined peaks were observed at Raman shifts of 1350 cm^{-1} (D-band), and 1580 cm^{-1} (G-

band), as well as a small peak at 2700 cm^{-1} (2D band) confirming the presence of graphene on the membrane surface. The Raman peak observed at around 700 cm^{-1} is due to the CF_2 bond stretching in the Nafion membrane.

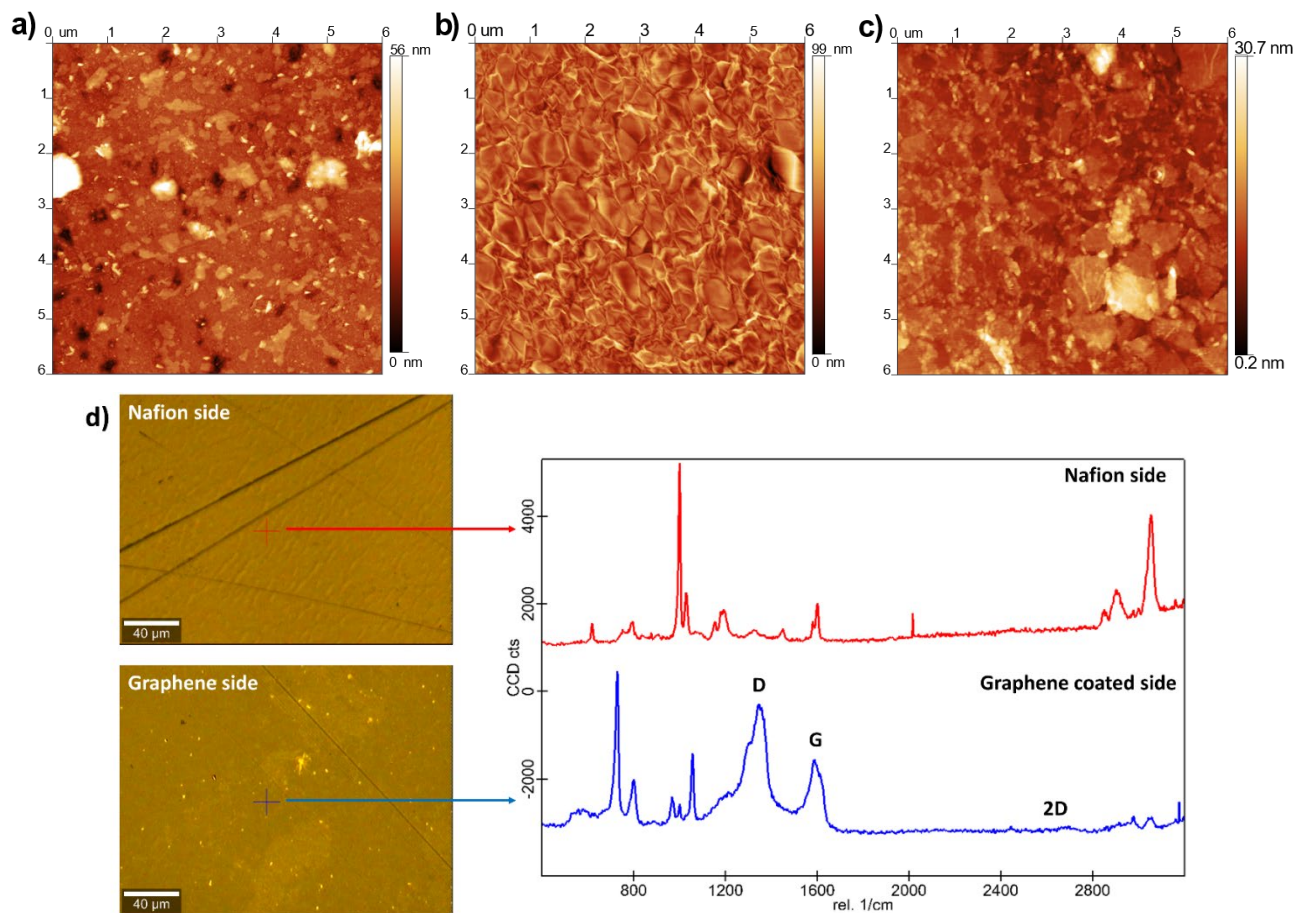


Figure 4. AFM images of a) top surface of uncoated Nafion, b) top surface of graphene coated Nafion, and c) top surface of mica coated with graphene; and (d) Raman spectra from the bare Nafion and graphene coated Nafion membrane.

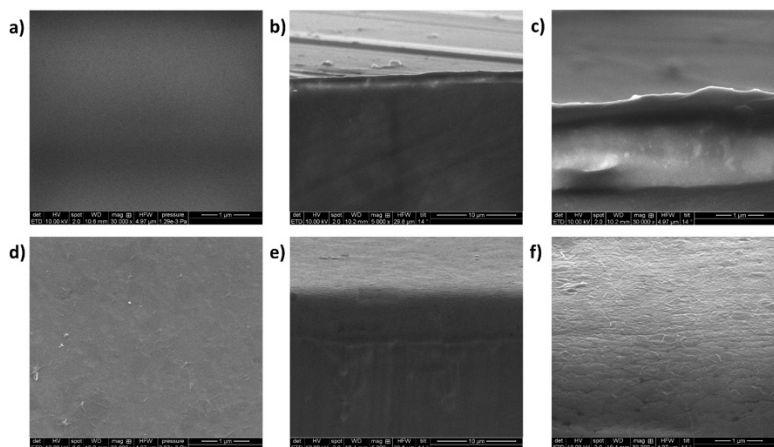


Figure 5. SEM images of: a) the surface of bare Nafion; b) & c) the cross section (14° tilt) of bare Nafion; d) the surface of graphene coated Nafion; e) & f) the cross section (14° tilt) of graphene coated Nafion.

In addition to these characterization methods, the vanadium permeability of the membranes was evaluated to investigate the expected impact of the coating on VRFB self discharge and battery cycling stability. In all cases, it was found that the graphene coating significantly reduced the vanadium permeability, and with increasing numbers of layers the crossover further decreased as expected.

Cation and anion exchange membrane samples suitable for RFB testing have been coated with graphene and tested to Calgary for testing including:

- Nafion 117 coated with one and two layers of NS-doped graphene coating on one side of the membrane, and with a single layer of graphene on both sides.
- Anion (Fumasep FAP-450) membranes coated with NS-doped graphene.
- Nafion membranes with lower thickness (Nafion 117, 115, and 212) coated (one side only) with NS-doped graphene

1.3 RFB performance data with a range of graphene coated membrane materials

A small bench-scale flow cell was used to study the VRFB charge–discharge. The cell used a graphite plate current feeder and a commercial ion-exchange membrane (with and without graphene coating). Initially, thermally treated (500 °C, 1 h in air) carbon paper was used as the cathode and anode electrodes. Standard charge-discharge experiments were carried out at current densities in the range 10 to 100 mA/cm², using cut-off cell voltages of 1.65 V on charge, and 0.8 V on discharge. The battery was run for at least two cycles at each current density to determine the current density performance relationship. The stability of the VRFB performance during long-term cycling at high current density is an important criterion that has been considered. Charge-discharge experiments were conducted at a relatively high current density (80 mA/cm²) for 100 cycles with and without graphene coated membrane. Each cycling stability experiment took from one to two weeks depending on the battery performance.

Experiments for a range of different coatings on commercial cation exchange membrane with different thicknesses: Nafion 117 (183 μm) and Nafion 115 (127 μm), with the arrangement of the coating on the

positive ($\text{VO}^{2+}/\text{VO}_2^+$) side of the battery has also been investigated. We also demonstrated the stability of the performance enhancement over 100 cycles of operation, with performance stability at least as good as an uncoated Nafion membrane. Self-discharge tests of some membranes were also been performed, to determine the impact of the graphene coating on vanadium cross-over. In addition to battery testing, we have also studied the membrane characterization of bare and graphene coated membranes.

Figure 6 shows the efficiencies (coulombic CE, voltage VE, and energy EE) of the battery during charge-discharge cycling of the VRFB at different current densities with graphene coated and uncoated Nafion 117 and 115. The battery performance results for the bare membranes are comparable with previous studies using the same electrode materials. The CE increased as the current density was increased from 10 to 100 mA cm^{-2} . With higher current density, the charge-discharge duration decreased; this leads to a decrease in the amount of crossover of vanadium species, and hence a higher CE. This trend confirms that vanadium species crossover is the main reason for CE losses. In addition, the use of a thinner membrane (Nafion 115) led to a lower CE than the thicker Nafion 117, confirming the vanadium permeability and self-discharge results. A higher CE was observed in the case of graphene coated membranes, since the graphene reduces the vanadium permeability without increasing the membrane thickness.

As the current density increases, the VE of the VRFB was observed to decrease (Figure 6c) due to increasing losses. Due to the lower area specific resistance of the thinner Nafion 115 membrane, around 2% higher VE was observed for this membrane than for Nafion 117. Although the area specific resistance of the graphene coated membranes was higher than their bare Nafion counterparts, the presence of the graphene coating led to a 10% and 5% higher VE for graphene coating on Nafion 117 and Nafion 115, respectively (Figure 6c), indicating that the total overpotential was reduced. The EE is the product of the CE and VE and was significantly higher for the graphene coated membranes than bare membrane at all current densities (Figure 6d). For example, the VRFB EE increased from 57% to 70% due to the graphene coating on Nafion 117 at a current density of 80 mA cm^{-2} . SEM and AFM images of the top surface of the graphene coated Nafion 117 before and after cycling confirmed the stability of the graphene layer on the membrane surface after cycling.

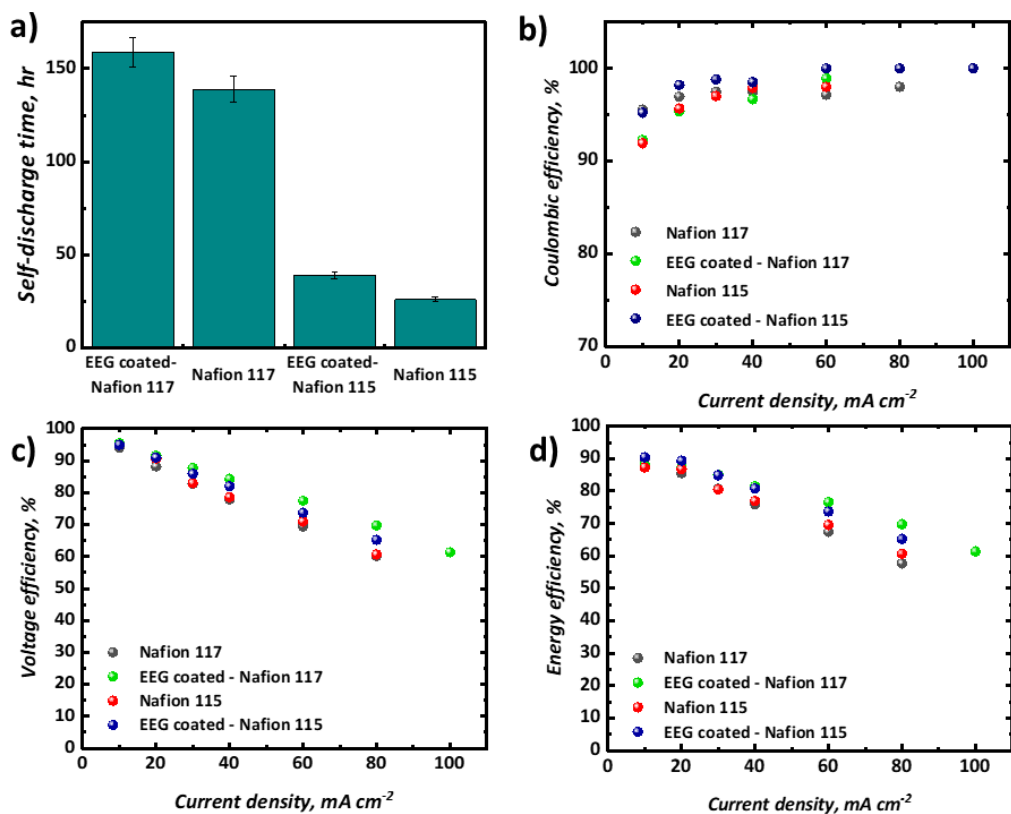


Figure 6. Comparison of VRFB performance using bare and graphene coated Nafion 115 and 117 membranes: (a) self-discharge curves at 50% SOC; and charge-discharge efficiencies at a range of current densities, including: (b) CE; (c) VE; and (d) EE.

To determine the power density, a polarization curve was obtained by measuring the battery voltage at a range of current density and at a selected state of charge (SOC, 100% SOC is a fully charged battery). The polarization curve and power density at 50% SOC for graphene coated and bare Nafion 117 and 115 membranes are shown in Figures 7a and 7b, respectively. The maximum power density delivered by the VRFB increased by 67% (from 150 mW cm^{-2} to 250 mW cm^{-2}) and 55% (from 114 mW cm^{-2} to 177 mW cm^{-2}) due to the graphene coating on Nafion 117 and Nafion 115, respectively. Electrochemical impedance spectroscopy (EIS) was also performed, which suggested that the mechanism for increased power density is lower charge transfer resistance. This indicates that the graphene was playing an active role in the electrochemical reactions, enhancing the electrode performance during discharge.

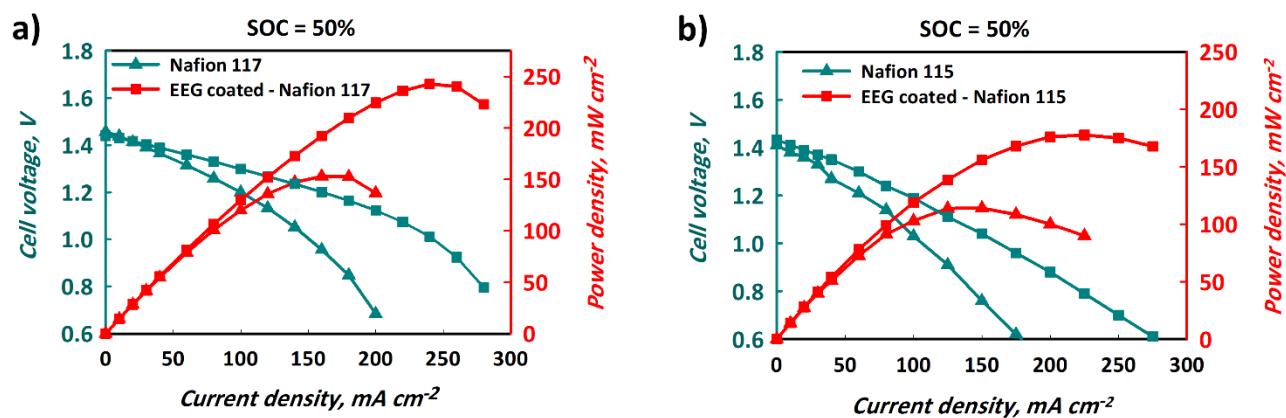


Figure 7. Polarization curves, for VRFB using uncoated and graphene coated Nafion membranes. Data is shown for (a) Nafion 117 and (b) Nafion 115.

Since the graphene was applied to a commercial Nafion membrane, the chemical and mechanical stability of the membrane during cycling was expected to be unaffected. However, the stability of the graphene coating was investigated, by evaluating whether the enhancement in VRFB performance observed was retained during long duration cycling. Figure 8 shows a comparison of the VRFB performance with graphene coated and uncoated Nafion membranes over 100 cycles of charge and discharge. The CE of the graphene coated membranes was close to 100% throughout the 100 cycles, due to the lower vanadium permeability of these membranes. The VEs and EEs of the VRFB show a slight decrease during cycling in all cases (Figure 8b and c). This is consistent with previous studies, and is due to decreasing electrochemical activity of the electrodes, most likely due to changes in the functional groups on the surface of the carbon paper. The enhancement in the VE and EE of the VRFB due to the graphene coating remains present after the 100th cycle, demonstrating the stability of the membrane coating. In addition, the capacity retention (Figure 9) was significantly higher for the graphene coated membranes, with discharge capacity retention of 73% and 65% of the initial capacity after 100 cycles (i.e. a discharge capacity loss of 0.27% and 0.35% per cycle) in the case of graphene coated Nafion 117 and Nafion 115, respectively. These rates of capacity fade are lower than the recently reported benchmark of 0.442% per cycle, and at the low end of the range of capacity fade rates in the literature. The results demonstrate that the presence of the graphene coating on the membrane enhances the stability of the battery operation and reduces the capacity fading due to vanadium crossover during cycling.

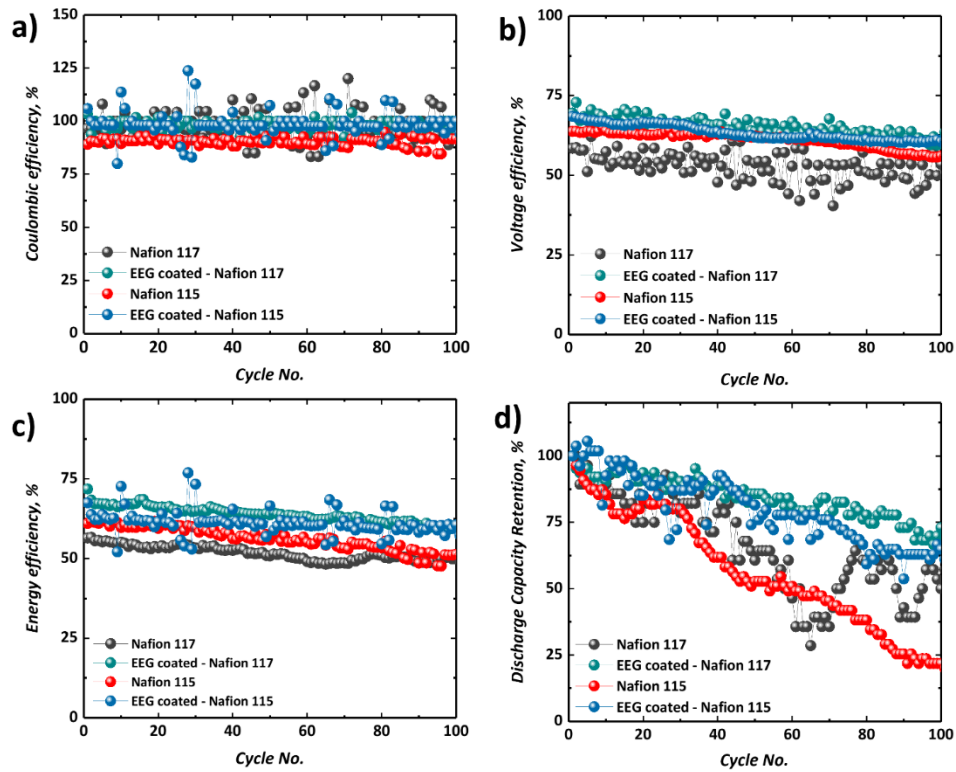


Figure 8. VRFB cycling stability, including: (a) CE, (b) VE, (c) EE, and (d) discharge capacity retention, during 100 cycles of VRFB charge-discharge at a current density of 80 mA cm^{-2} , using graphene coated and uncoated Nafion membranes.

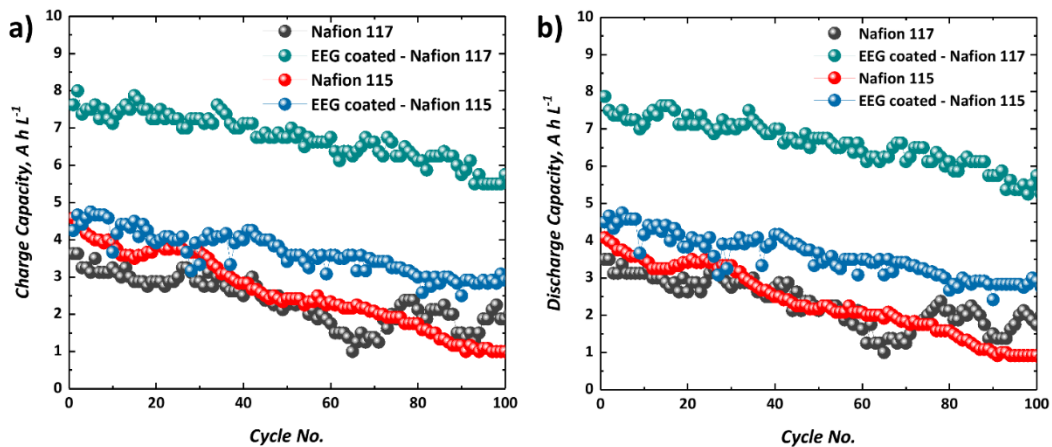


Figure 9. a) Charge, b) Discharge capacity over the VRFB cycling with graphene coated and bare membrane at current density of 80 mA cm^{-2} .

Anion exchange membrane (AEM)

The membrane coating optimization was different for an anion exchange membrane. In this case, the highest power density was obtained when a graphene coating was applied to both sides of the membrane.

As shown in Figure 10, the maximum power density delivered by the VRFB increased by around 70% (from 100 mW cm^{-2} to 170 mW cm^{-2}) due to the graphene coating on both side AEM.

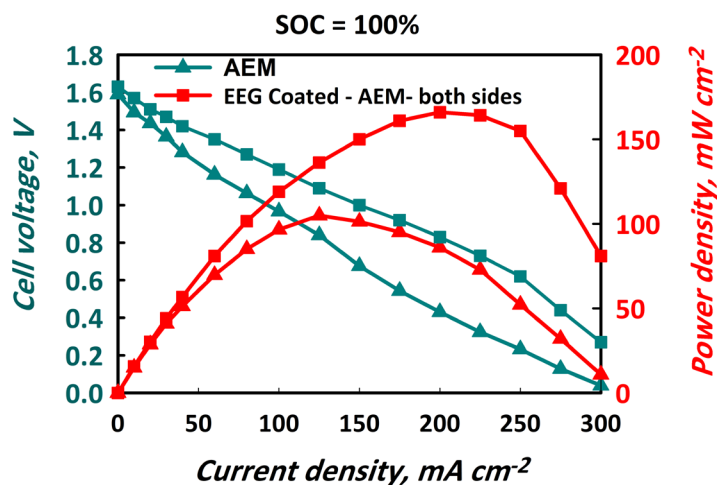


Figure 10. Polarization curves for VRFB using uncoated and both sides graphene coated AEM.

VRFB Performance with Graphite Felt Electrodes

During the final year of the project, a collaboration was established with a leading VRFB company. They were interested to test our membrane, and we prepared samples of uncoated and coated membranes to enable them to perform a like-for-like comparison of the membrane in their labs. Unfortunately they found no difference in power density between the coated and uncoated membranes. This was a surprise, as our side by side testing had consistently delivered higher power density with the coated membrane. After reviewing the findings with our VRFB collaborator, it was determined that the main difference in their set up was the use of graphite felt electrodes, while we were using carbon paper. Graphite felt electrodes have a higher surface area and enable higher power density than carbon paper. We had consistently used carbon paper as the power supplies we were using could not deliver sufficient current to enable operation at the higher currents used with graphite felt. In order to determine if the use of graphite felt electrodes would explain the different findings, we modified our setup and obtained a high current power supply in order to evaluate the VRFB performance with coated membranes and graphite felt electrodes.

After optimizing the cell design, electrode pretreatment, and operating conditions, we were able to reproduce the findings from our VRFB industry partner. As shown in Figure 11, with graphite felt electrodes the charge discharge efficiencies of VRFB using graphene coated electrodes is almost exactly the same as that with an uncoated membrane. The graphene coating led to a slightly higher CE, indicating less vanadium crossover, and slightly lower VE, due to increased membrane resistance. The polarization behavior (Figure 12) shows that with the graphene coating the maximum power density of the VRFB is slightly lower. It should be noted that with graphite felt electrodes the maximum power density of the VRFB is around 2.5 times higher than that obtained with carbon paper electrodes.

Consistent with the EIS results, it was concluded that the increased power density observed with carbon paper electrodes was due to active participating of the graphene in the electrochemical reactions. This led to a reduction in the charge transfer resistance, higher voltage efficiency and enabling operation at higher current density (and hence higher power density). However, with graphite felt electrodes, it appears that the charge transfer resistance is very low, and any reduction in the charge transfer resistance thus has no effect on the maximum power density. In this case, the maximum power density appears to be limited by ohmic rather than charge transfer resistance.

In spite of these disappointing results, Invivity remain interested in the coated membrane, as they observed that it enhances the cycling stability of the battery without reducing the power output. This provides an alternative opportunity for graphene coated membrane. Further work is needed at lab scale to optimize the coated membrane to enhance cycling stability, as opposed to power density.

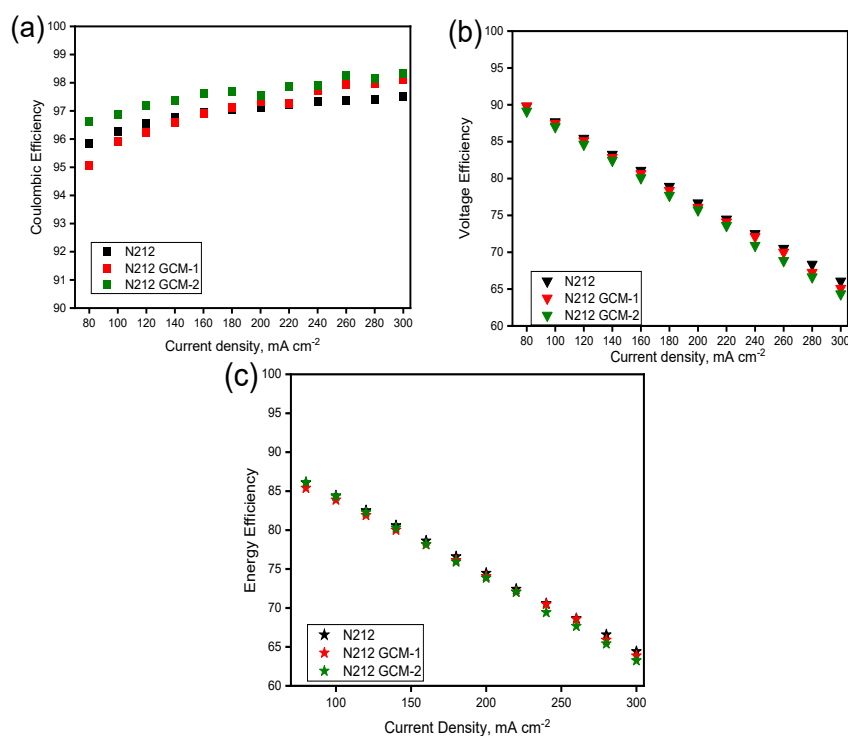


Figure 11. Comparison of VRFB efficiencies using graphene felt electrodes, with bare and Graphene-coated Nafion 212 at a range of current densities, including (a) CE, (b) VE, and (c) EE.

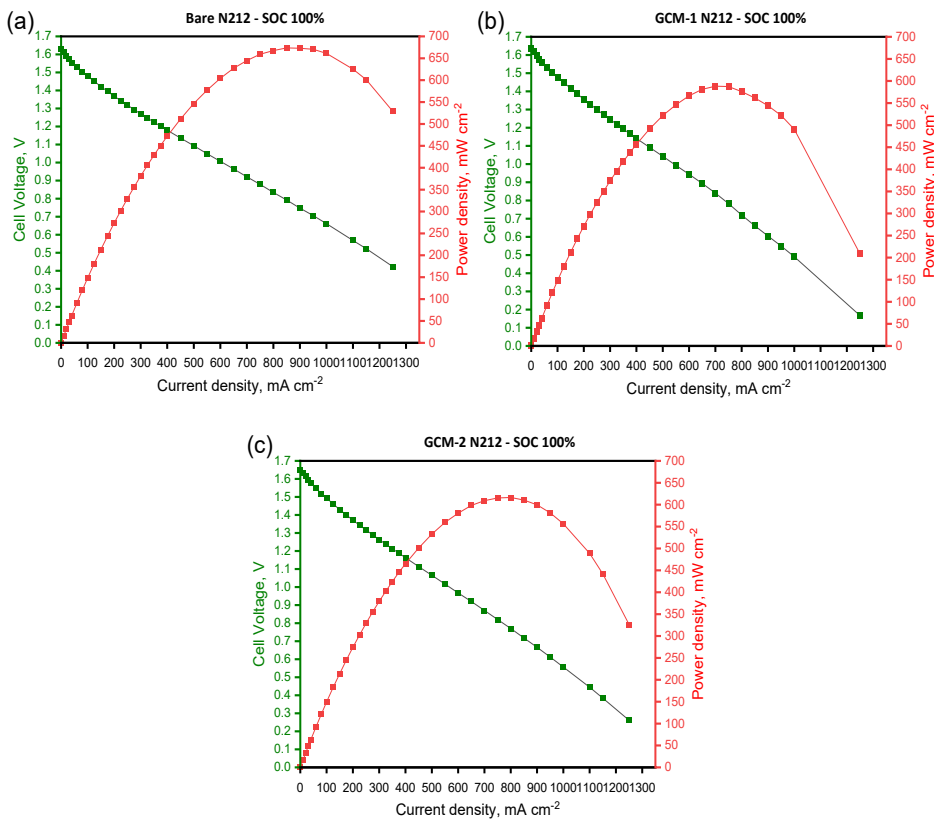


Figure 12. Comparison of Polarization curves @ SOC 100% for (a) uncoated, (b) single side and (c) both sides graphene-coated Nafion.

2. Evaluation of other Redox Flow Battery Chemistries

2.1 Zinc Iodide redox flow battery

The performance and cyclability of a zinc iodide flow battery using a Nafion membrane 117 coated with graphene, with varying types of graphene loading has been investigated. Different coatings, including 1 graphene layer on both sides, 2 layers on the iodine side and 1 layer on the zinc side, and 2 layers on both sides of the membrane, were tested in the battery. Due to a higher hydrophobicity of the membrane coated with graphene, the problem of unbalanced volume of electrolyte in the zinc iodide battery is eliminated compared with the battery with an uncoated membrane. Improved battery performance was obtained, with the best results using a membrane coated with on layer of graphene on both sides.

The results of the performance, cyclability, and EIS analysis of a zinc-iodide flow battery using graphene coated membranes are presented in Figure 13. A battery with a graphene coating on both sides demonstrated improved performance (3-5% increase in charge discharge efficiency) and similar stability during cycling compared to an uncoated membrane, as shown in Figure 13a. It was also observed that the battery with graphene coating on both sides had lower ohmic and charge transfer resistance during cycling when compared to uncoated membrane. This improvement in performance may be attributed to the higher conductivity of the membrane with graphene coating (shown in Figure 13b). A stable charge

efficiency of approximately 90-95% was observed in a sample where the two layers of graphene were applied on the iodine side and one layer the zinc side. The voltage efficiency of this sample was found to be similar to that of the baseline uncoated samples (see Figure 13c).

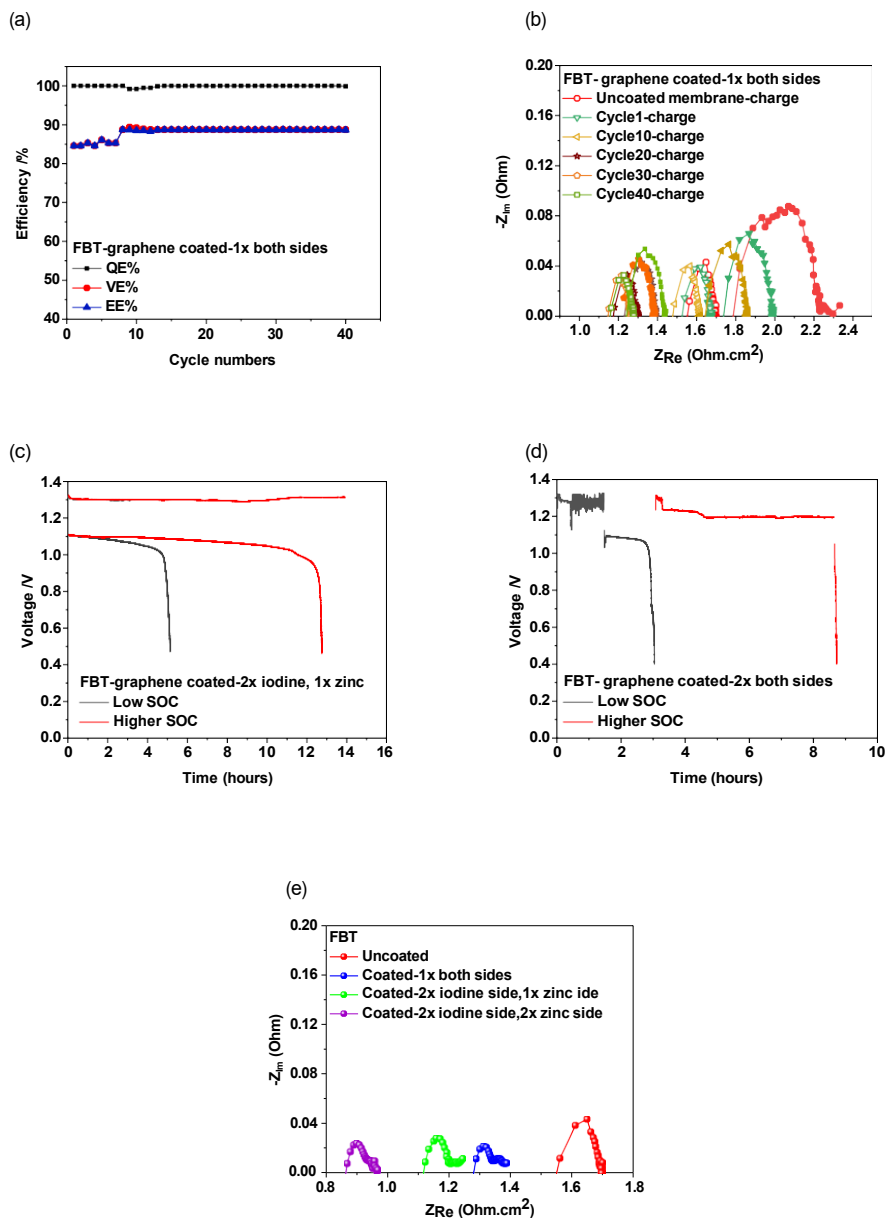


Figure 13. Performance and cycling stability of zinc iodide flow battery with 3M ZnI with graphene-coated Nafion 117 **(a)** cycling stability 1 layer graphene on both sides, **(b)** ohmic and charge transfer resistances during the cycling, **(c)** charge-discharge curves for 27.5% and 55% SOC, **(d)** performance with the membranes 2x coated on both sides, **(e)** EIS analysis of various of graphene coatings at SOC of 27.5%.

2.2 All-iron RFB

A flow cell with an interdigitated flow field was used to study the all-iron RFB charge–discharge. The cell used a graphite plate current feeder and a Nafion cation exchange membrane (with and without graphene coating). Thermally treated (500 °C, 1 h in air) carbon paper was used as the cathode and anode electrodes. A potentiostat operating in galvanostatic mode was used to control the charge-discharge experiments. The duration of each charge-discharge experiment is around 12 hours for current density 10 mA/cm², respectively. Thus, performing a set of charge-discharge cycling experiments on a single membrane with current density of 10 mA/cm² took around two to three weeks of continuous operation. An all-soluble, all-iron redox flow battery was conducted by using a ferrocyanide-based polysolite, and a negolyte containing a hydroxylamine-based iron complex electrolyte. The performance and cyclability of the all-iron flow battery using a Nafion membrane 117 coated with graphene, with varying types of graphene loading was investigated. Different coatings, including 1 graphene layer on both sides, and 1 layer on the positive side were tested in the battery. Improved battery performance was obtained, with the best results using a membrane coated with one layer of graphene on both sides.

A significant higher capacity and capacity retention over the cycling in the case of both side coated N117 was observed (see Figure 14). A single layer of graphene on each side decrease the iron crossover during cycling and increase the cyclability of the battery. A single layer of graphene in front of positive side had a negligible improvement effect on the battery performance and capacity retention over the cycling.

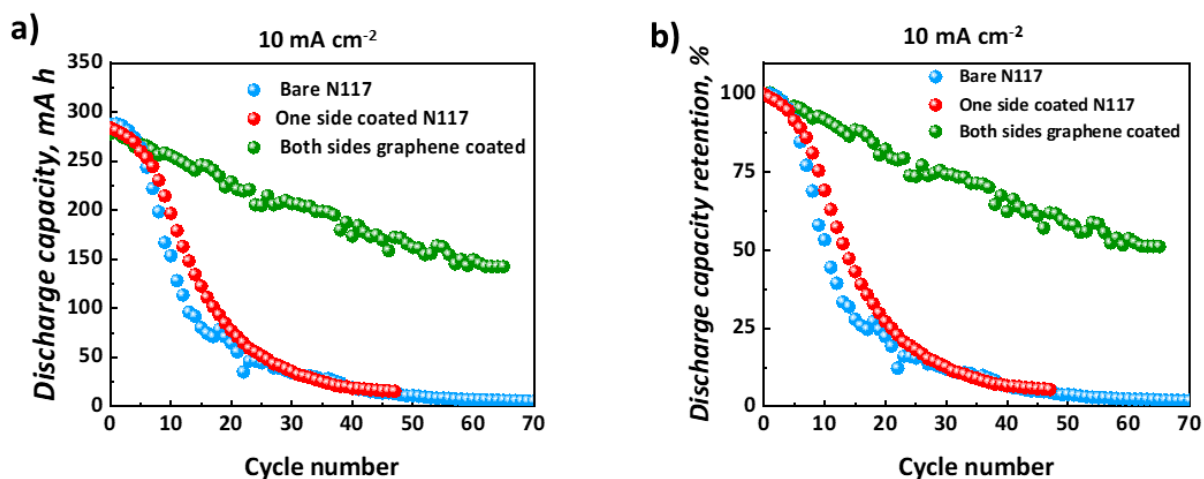


Figure 14. a) Discharge capacity, b) Discharge capacity retention over the all-iron RFB cycling with graphene coated N117 membrane at current density of 10 mA cm⁻².

3. Scale-up of graphene production from gram to kilogram scale

3.1 Large scale batch graphene production process – construction and commissioning

Laboratory scaleup was evaluated using a 16 cm² (4 cm x 4 cm) electrode, including either one or two counter electrodes. The data from these experiments was used to generate estimates of the requirements for a larger electrode area of 900 cm² (30 cm x 30 cm) for the large-scale batch reactor. The design and

construction of a 2 kg per day electrochemical reactor was completed. The design includes a feed pump that pumps the electrolyte (0.1M $(\text{NH}_4)_2\text{SO}_4$) into the reactor, and a heat exchanger for temperature control (see Figure 15). The reactor was constructed using 3D printing technique. The reactor design and process flow diagram for the reactor setup was completed using CFD simulations and models. The power consumption of the reactor is approximately 3 kW at maximum operating conditions, leading to heating during the exfoliation process. This heat could have an impact on the exfoliation process including changes in the electrolyte volume due to evaporation, and changes in the graphene functional groups. Thus, there is a need for the reactor to have a setup to control and monitor its temperature. Hence, a heat exchanger unit is necessary to control the heat generated and the temperature of the electrolyte during the exfoliation process. The flow characteristics of the reactor were studied using computational fluid dynamics simulations to obtain a design that ensures the desired flow conditions in the reactor. Six different geometries were compared to observe the flow pattern and identify any stagnant zones with very low mixing.

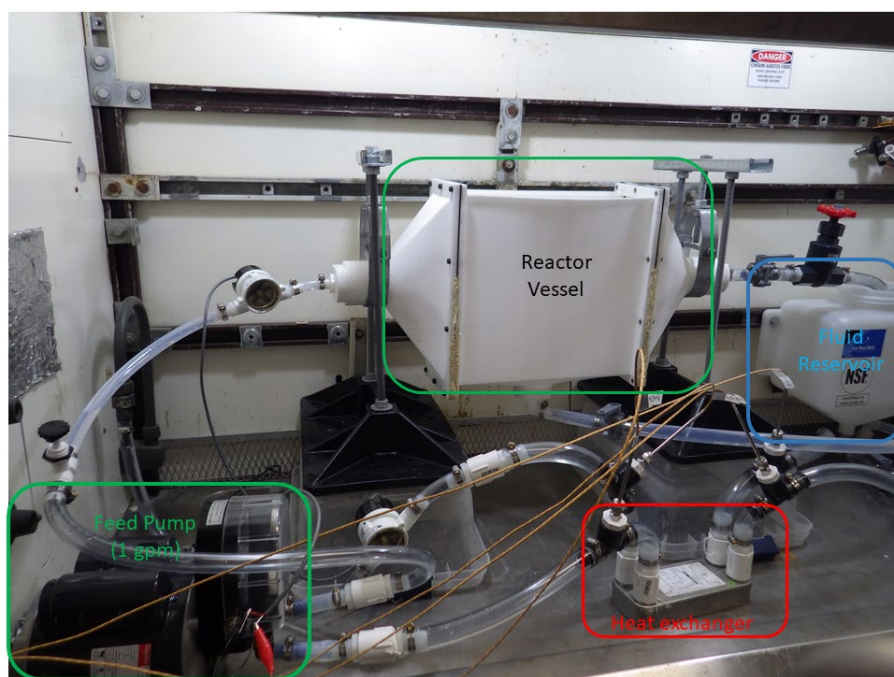


Figure 15. The reactor setup and flow circuit including the heat exchanger, feed pump, and fluid reservoir.

3.2 Large scale batch graphene production process – design and operating conditions

The reactor operating conditions were first optimized to enhance the yield of graphene until a yield similar to that obtained in the small scale exfoliation experiments. This required modifications to the reactor components and the electrode geometry.

The specific surface and the electrical conductivity of the graphene was similar but slightly lower than that obtained using a small scale reactor. The quality of the graphene product is sufficient for preparing

commercial scale quantities required for coated membrane production, however it is likely that further iteration and optimization of the reactor design and operating conditions is possible.

4. Evaluation of Modified Membranes in a 5 kW Commercial Redox Flow Battery

4.1 Roll-to-roll coating of membrane

The best performing graphene materials were formulated into an ink (NP) for initial trials on a scale-down version of Evercloak's roll-to-roll system (65 mm coater). Instead of using expensive Nafion films, these initial trials were carried out using inexpensive polyethylene terephthalate (PET) substrates. A picture of the small-scale roll-to-roll system in action is shown in Figure 16a. The graphene ink, which is injected on the surface of the water, leaves floating graphene sheets on water while the spreading force of each drop pushes and compresses the film against the withdrawn substrate. The graphene film was found to form as expected but the film did not adhere well to the PET (see dark "patchiness" on the film as shown in Figure 16) – likely due to insufficient wetting properties. The soaked Nafion is expected to provide much more hydrophilic support and we don't expect significant challenges with that substrate. However, if continuous coating poses a challenge, we have also come up with an alternative solution which is to use a larger-scale continuous coater in a batch mode. The dimensions of the coated membrane are suitable for installing in the commercial scale RFB. Subsequently, the team used plasma-treated biaxially oriented polypropylene which was a substrate with more favorable wetting qualities. As shown in Figure 16c), the small, single nozzle roll-to-roll system was able to coat a uniform and continuous layer on this more hydrophilic sample that better mimics the hydrophilicity of the Nafion membranes.

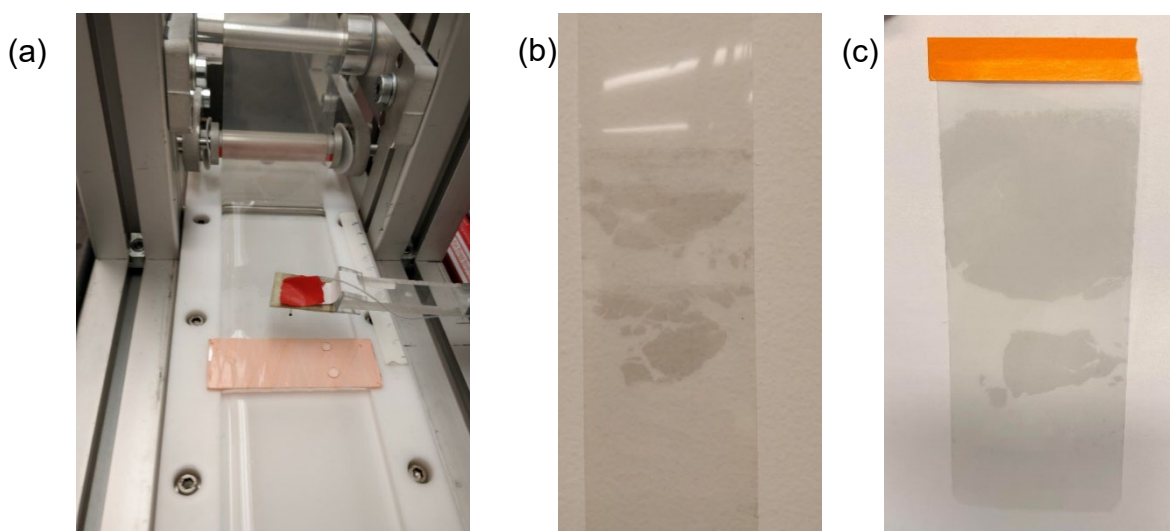


Figure 16: a) Roll-to-roll system; b) PET film showing unstable graphene film transfer (patches detached and slid down PET during withdrawal). c) Plasma treated BOPP substrate with improved hydrophilicity coated with a nearly continuous layer of graphene

With this successful proof of concept, the team moved towards using a larger width (8") continuous coater with three nozzles to inject the graphene ink on the air-water interface. The distance between nozzles to create a coherent film is determined by the spreading profile of the solvent and by how far and with how much force the solvent spreads driven by Marangoni-like flows. A schematic of the system showing the three nozzles is shown in Figure 17a). Using this system, we first started by creating graphene coatings in a semi-batch mode where the films was continuously laid down by the three nozzles but the floating films was not transferred and only used to cover an $\sim 8'' \times 8''$ area. A slightly smaller piece of glass ($\sim 7'' \times 7''$) was placed beneath the water and the film lowered onto the substrate by removing water from the coating bath. By placing some small squares of mica on the glass, we were able to image the resulting graphene film and confirmed that the film morphology was similar to those made using the batch Lanmguir-Blodgett trough used to coat the Nafion substrates for our initial investigations (see inset of Fig. 17b)). Ultimately, this same system was used to coat 8" wide Nafion sheets continuously. However, coating these large area substrates was not pursued further due to the decision not to proceed with commercial VRFB testing.

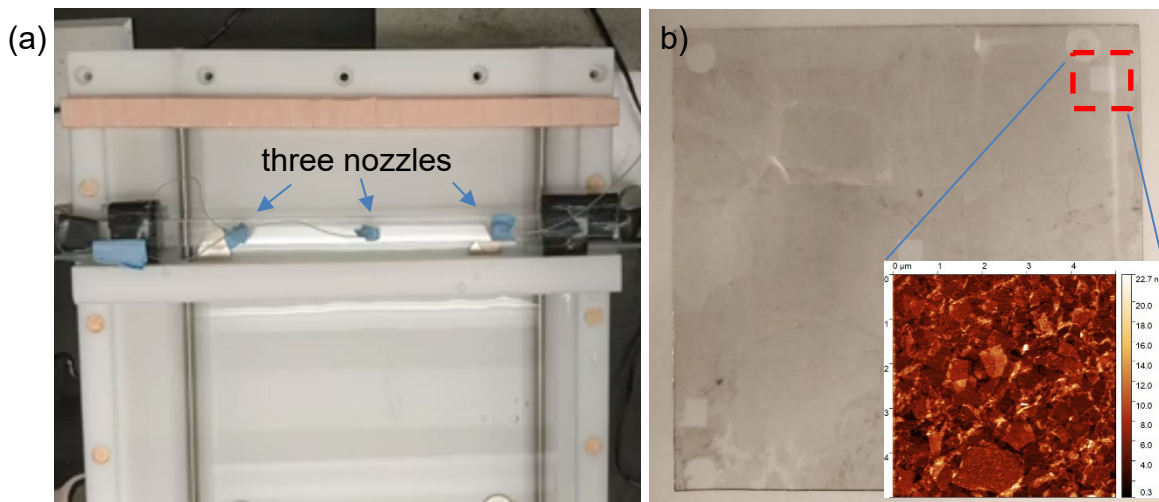


Figure 17: a) Photograph of 8" roll-to-roll coater with three nozzles set-up to inject the graphene ink onto the air-water interface; b) Photograph of 7" \times 7" glass piece coated with the three-nozzle system with inset showing and AFM image of the resulting film deposited on mica place atop the glass.

4.2 Operation of 5 kW commercial VRFB

Figures 18 and 19 show the 5 kW commercial VRFB that was installed and operated. This included splitting the electrolyte and performing an initial charge and discharge of the battery.



Figure 18. The 5 kW commercial VRFB with power supply and load equipment for charge-discharge battery.



Figure 19. The 5 kW commercial VRFB.

F. KEY LEARNINGS

Please provide a narrative that discusses the key learnings from the project.

- Describe the project learnings and importance of those learnings within the project scope. Use milestones as headings, if appropriate.
- Discuss the broader impacts of the learnings to the industry and beyond; this may include changes to regulations, policies, and approval and permitting processes

RESPOND BELOW

Laboratory Scale Optimization

Studies of the operating conditions for the graphene production and membrane coating processes provided new insights into the impact on redox flow battery performance. For VRFBs using carbon paper electrodes, significant (>50%) enhancement in the battery power density can be achieved by using a graphene coated membrane. The graphene processing and coating conditions were optimized to maximise the power density and performance in this case. For VRFBs using graphite felt electrodes, the membrane coating did not improve the power density of the battery. However, for both electrode systems, the coated membrane improved the stability of VRFB operation, decreasing capacity decay due to lower vanadium crossover through the membrane.

The membrane was also tested in two other flow battery chemistries: a zinc-iodide hybrid flow battery, and an all-iron RFB. In all cases the graphene coated membrane offered improvements in battery performance. However, the optimum membrane coating was different for each chemistry, and the main benefit was reduced crossover and enhanced cycle stability.

Scale-up

The scalability of the graphene production and coating process was demonstrated at bench scale. It is clear that these technologies can be readily scaled to enable large scale production of graphene coated membranes for application in commercial batteries. However, most if not all commercial RFBs use felt electrodes, and as no increase in power density was obtained in this case, testing of the technology in a commercial battery cannot be justified at this stage. Further laboratory work is needed to optimize the technology to reduce crossover and increase cycle stability in VRFB and other RFB chemistries. In addition, techno-economic evaluation of the benefits of increased cycle stability with the graphene coated membrane is needed. There is currently insufficient data to evaluate the commercial potential of the technology for this application. It is recommended that further laboratory studies are carried out and evaluated in partnership with RFB companies to determine the potential of the technology.

G. OUTCOMES AND IMPACTS

Please provide a narrative outlining the project's outcomes. Please use sub-headings as appropriate.

- **Project Outcomes and Impacts:** Describe how the outcomes of the project have impacted the technology or knowledge gap identified.
- **Clean Energy Metrics:** Describe how the project outcomes impact the Clean Energy Metrics as described in the *Work Plan, Budget and Metrics* workbook. Discuss any changes or updates to these metrics and the driving forces behind the change. Include any mitigation strategies that might be needed if the changes result in negative impacts.
- **Program Specific Metrics:** Describe how the project outcomes impact the Program Metrics as described in the *Work Plan, Budget and Metrics* workbook. Discuss any changes or updates to these metrics and the driving forces behind the change. Include any mitigation strategies that might be needed if the changes result in negative impacts.
- **Project Outputs:** List of all obtained patents, published books, journal articles, conference presentations, student theses, etc., based on work conducted during the project. As appropriate, include attachments.

RESPOND BELOW

Project Outcome and Impacts

The insights provided by the project have enabled us to target a new direction for the development of membranes for VRFBs. It is clear that the role of the membrane cannot enhance the electrode performance in order to increase power density in commercial batteries for renewable integration and grid stabilization. However, development and optimization of membranes to reduce crossover and enhance cycle stability can reduce the operating and maintenance cost of VRFBs for energy storage. In addition, the use of a graphene coating to reduce crossover may enable the use of thinner membranes with lower resistance, which will enable higher power density while meeting commercial crossover targets. This will reduce the battery cost and enhance the viability of this important clean technology.

Clean Resources and Program Specific Metrics

The following Metrics have been achieved during the project:

- Through this project, clean technology company Bee Energy Inc. has been launched. Bee Energy is developing and commercializing graphene production technology, aiming to enable its customers to deliver sustainable solutions such as high performance next generation batteries, and strong lightweight composite materials. The company is also aiming to pursue commercialization of graphene coated membrane materials for batteries and other applications such as water treatment.
- During the project, clean technology company Bee Energy Inc. raised seed investment to commercialize graphene production technology.

- The TRL level of graphene production technology has been advanced from TRL 4 to 5. The goal of TRL 5 was not achieved as the decision was taken not to pursue evaluation of the technology in a commercial battery at this time.
- Collaborations between the University of Calgary and four clean technology industry partners are on-going: StorEn Inc. (VRFB company), Evercloak Inc. (membrane company), a leading VRFB (confidential) and Bee Energy Inc. (graphene production startup).
- Knowledge mobilization has been achieved through social media (LinkedIn) news announcements, conferences, participation in events (e.g. the Advanced Materials Show and Graphene Technology Conference), the technology was also promoted at two Innovation Fairs at the University of Calgary.

Although scale up of the technology is not currently being pursued, the technology still has the potential to enable enhanced battery performance for renewables integration and grid stabilization.

Project Outputs

Journal Articles:

Maedeh Pahlevaninezhad, Elizabeth Esther Miller, Lixin Yang, Lauren Sarah Prophet, Ashutosh Singh, Thomas Storwick, Majid Pahlevani, Michael A. Pope, and Edward P. L. Roberts, 2023, Exfoliated Graphene Composite Membrane for the All-Vanadium Redox Flow Battery. *ACS Applied Energy Materials* 6(12), 6505–6517.

Damilola Momodu, Moshawe J. Madito, Ashutosh Singh, Farbod Sharif, Kunal Karan, Milana Trifkovic, Steven Bryant, Edward P.L. Roberts, 2021, Mixed-acid intercalation for synthesis of a high conductivity electrochemically exfoliated graphene. *Carbon*, 171, 131-140.

Conference Publications and Presentations

Maedeh Pahlevaninezhad, Ashutosh Kumar Singh, Thomas Storwick, Elizabeth Esther Miller, Anne Yang, Majid Pahlevani, Michael Pope, Edward PL Roberts, 2022, An Advanced Composite Membrane for the All-Vanadium Redox Flow Battery. *ECS Meeting Abstracts* MA2022-01 466. Presented at the 241st meeting of the Electrochemical Society, May 2022, Vancouver, Canada.

Edward Roberts, Mohammad Rahimi, Asghar Molaei Dehkordi, Fatemeh ShakeriHosseinabad, Maedeh Pahlevaninezhad and Ashutosh Kumar Singh, 2022, Redox Flow Battery Innovation. *ECS Meeting Abstracts* MA2022-01 483. Invited talk, presented at the 241st meeting of the Electrochemical Society, May 2022, Vancouver, Canada.

Roberts, Edward P.L. (2022) *Emerging Chemistries and Materials for High-Energy Density Redox Flow Batteries*, Invited presentation, International Battery Seminar, Orlando FA, USA, March 2022.

Patent application (published 2021):

E Roberts, A Singh, Electrochemical graphene exfoliation with hydroxide intercalation. US Patent App. 17/174,552.

H. BENEFITS

Please provide a narrative outline the project's benefits. Please use the subheadings of Economic, Environmental, Social and Building Innovation Capacity.

- **Economic:** Describe the project's economic benefits such as job creation, sales, improved efficiencies, development of new commercial opportunities or economic sectors, attraction of new investment, and increased exports.
- **Environmental:** Describe the project's contribution to reducing GHG emissions (direct or indirect) and improving environmental systems (atmospheric, terrestrial, aquatic, biotic, etc.) compared to the industry benchmark. Discuss benefits, impacts and/or trade-offs.
- **Social:** Describe the project's social benefits such as augmentation of recreational value, safeguarded investments, strengthened stakeholder involvement, and entrepreneurship opportunities of value for the province.
- **Building Innovation Capacity:** Describe the project's contribution to the training of highly qualified and skilled personnel (HQSP) in Alberta, their retention, and the attraction of HQSP from outside the province. Discuss the research infrastructure used or developed to complete the project.

RESPOND BELOW

The focus of the project has been on research and development of innovative technology. While the project has yielded valuable research findings, contribution of economic, environmental and social benefits to Alberta have been limited. A start-up company has been launched to commercialize the graphene production technology, and the graphene coated membrane may be one produce line for this company. The insights provided by the project findings has enabled the company to direct the development of the membrane technology to suitable applications, and to focus its main commercialization goals on other applications of graphene such as lithium battery electrodes.

The project has supported the training of 8 HQP at the University of Calgary, including 2 postdoctoral fellows, 3 PhD, 2 MSc students and 1 undergraduate student (summer research internship). All of the graduate and postdoctoral researchers were originally attracted to Calgary from outside the province.

The project used extensive technical infrastructure at the University of Calgary including:

- Electrochemical engineering laboratory facilities, including RFB test stations, electrochemical workstations, benchtop and high capacity centrifuges, four point probe conductivity meter, and other standard laboratory instruments (e.g., pH meters, power supplies, etc.);
- Materials characterization instruments including a Raman microscope, atomic force microscope, contact angle measurement, dynamic light scattering analyzer, thermogravimetric analyzer, scanning electron microscope, and transmission electron microscope.

- The unique 20 kW research microgrid facility, including the 5 kW StorEn VRFB.

In addition, a transmission electron microscope and x-ray photoelectron spectrometer at the University of Alberta's NanoFab facility was used for characterization of graphene samples.

I. RECOMMENDATIONS AND NEXT STEPS

Please provide a narrative outlining the next steps and recommendations for further development of the technology developed or knowledge generated from this project. If appropriate, include a description of potential follow-up projects. Please consider the following in the narrative:

- Describe the long-term plan for commercialization of the technology developed or implementation of the knowledge generated.
- Based on the project learnings, describe the related actions to be undertaken over the next two years to continue advancing the innovation.
- Describe the potential partnerships being developed to advance the development and learnings from this project.

RESPOND BELOW

It is recommended to undertake further laboratory work to optimize the graphene coating technology to reduce crossover and increase cycle stability in VRFB. In addition techno-economic evaluation of the technology is needed to evaluate the impact of the membrane modification on capital, maintenance and operating costs.

Further laboratory testing is planned using existing NSERC funded projects before pursuing commercialization of the technology. Collaboration with the University of Waterloo, Evercloak Inc., and Bee Energy Inc. to develop the optimum membrane modification process for VRFB applications, based on our new understanding of the role of the membrane. This will include evaluation of the cost of the coating. Collaboration with StorEn and another international VRFB company will continue in order to evaluate the potential of the membrane technology, and its performance in commercial VRFBs. In particular, the potential impact of the membrane on operating and maintenance costs will be evaluated. In addition, the use of the membrane coating to enable the use of thinner membranes in VRFB to achieve higher power density will be explored through these collaborations.

J. KNOWLEDGE DISSEMINATION

Please provide a narrative outlining how the knowledge gained from the project was or will be disseminated and the impact it may have on the industry.

RESPOND BELOW

The knowledge gained from the project has and is being disseminated by a number of mechanisms:

- Project findings are shared with the industry partners, through regular project updates and meetings.
- Ashutosh Singh, a postdoc who working on the project with extensive knowledge of the technology, is CEO of graphene start-up company Bee Energy Inc.
- A new collaborations with a leading international VRFB company, has been established. Project findings have been shared with VRFB experts at the company to share the project findings. Samples of graphene coated membranes have been sold to the company for testing.
- The project findings have been presented at international academic conferences and at battery events such as the International Battery Seminar.

Bee Energy Inc. are pursuing applications of the graphene product we have developed for battery and other applications. The direct impact of the project on the battery industry will depend on future developments of the membrane technology for increasing cycling stability in VRFB and other emerging RFB battery chemistries.

K. CONCLUSIONS

Please provide a narrative outlining the project conclusions.

- Ensure this summarizes the project objective, key components, results, learnings, outcomes, benefits and next steps.

RESPOND BELOW

The original objective of the project was to develop an innovative membrane modification to enhance the performance of VRFB for energy storage, in particular by increasing the battery power density. Although the technology was developed and optimized to achieve a significant increase (>50%) in the power density of laboratory VRFBs, it was determined that similar enhancement would not be achieved in commercial VRFB. Unexpectedly, it was found that the enhancement achieved was dependent on the electrode material used in the cell. With the graphite felt electrodes used in commercial VRFB, no enhancement in power density was obtained with the modified membrane. In spite of this, it was found that the graphene coated membrane could significantly reduce vanadium crossover, enhancing the cycling stability, without

decreasing the battery efficiency or power density. This is an important benefit, and further work is needed to develop and optimize the membrane coating process for this application.

The project provided new insights into the graphene production and membrane coating processes, and the application of graphene coated membranes to VRFBs and other battery chemistries. Based on these insights, a new strategy has been identified for the development of innovative composite membranes that can deliver improved performance in commercial RFBs, reducing their capital and operating cost. Furthermore, the scalability of the technology was demonstrated, giving confidence that the technology can be used for commercial scale applications.