

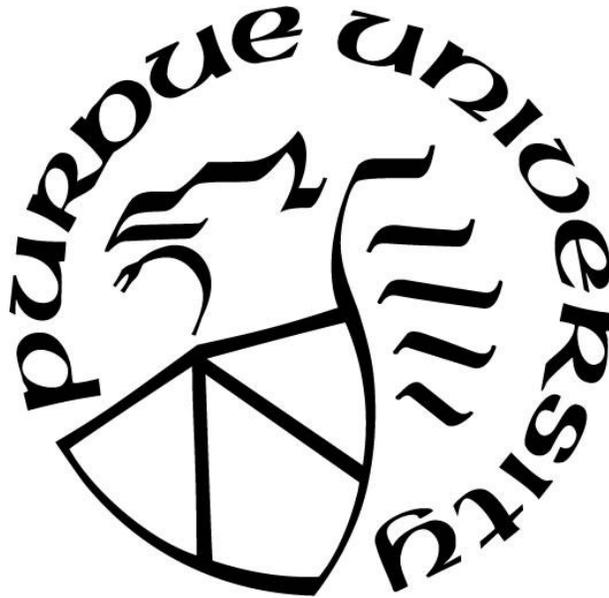
**DEVELOPMENT OF MODIFIED SEPARATOR USING VERMICULITE
FOR SAFER LITHIUM-ION BATTERIES**

by
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LIST OF ABBREVIATIONS

BET	Brunauer, Emmett, and Teller
DSC	Differential scanning calorimetry
EDS	Energy-dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
LCO	Lithium cobalt oxide
LFP	Lithium iron phosphate
LIB	Lithium-ion battery
LMO	Lithium manganese oxide
MMC	Multimode calorimetry
NMP	N-Methyl-2-Pyrrolidone
NMC	Lithium nickel manganese cobalt oxide
PE	Polyethylene
PP	Polypropylene
PVdF	Polyvinylidene Fluoride
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
TGA	Thermal gravimetric analysis
XRD	X-ray diffraction

ABSTRACT

Lithium-ion batteries (LIBs) have been used in portable device application for decades because they are lightweight and can store a high amount of energy. Consequently, they pose a risk if mechanically, electrically, or thermally abused. A thermal runaway occurs when the exothermic reactions propagate uncontrollably, usually ending in a cell burst. Commercially, the components used in a LIB do not aid in the thermal runaway and can ultimately act as catalysts. One factor that can result in a short-circuit and thermal runaway is internal contact between the electrodes. Usually, these are separated by a polymer separator made of polypropylene (PP) or polyethylene (PE). These compounds can start shrinking past temperatures of 130°C, providing spaces for the electrodes to touch, resulting in an exothermic reaction. This research explores a fire-retardant mineral, vermiculite, in combination with polyvinylidene fluoride (PVdF), a common binder in electrode and separator fabrication, as a PP separator modification.

Results indicated enhanced thermal stability while maintaining comparable electrochemical performance. After performing several characterization experiments on the vermiculite to understand its structure and composition, it was ground into a powder and fabricated into a slurry with PVdF. Initial iterations suggested that a thicker vermiculite ratio and application layer demonstrated high capacity fade and therefore required optimization. It was discovered that a 1:10 ratio of vermiculite to PVdF applied on PP with a thickness of 7 μ m maintained comparable capacity and ionic conductivity to the pristine PP cells. The voltage profiles demonstrated similar charging and discharging plateaus at ~3.46 V and ~3.40 V respectively. The modified and pristine separators were subjected to thermal stability tests such as differential scanning calorimetry (DSC) and multimode calorimetry (MMC). The DSC results demonstrated a 3.38°C higher melting temperature for the modified separator. When assembled into cells and subjected to MMC testing, the modified separator cell produced less exothermic energy release than the pristine separator cell, indicative of a safer cell during thermal runaways.

1. INTRODUCTION

June 2008: a laptop catches on fire in a conference in Japan [1]. September 2010: a Boeing cargo plane caught fire in Dubai [1]. January 2016: a Tesla caught on fire while fast charging in Norway [2]. From 2006-present: tens of thousands of mobile phone have exploded or caught on fire [1]. While lithium-ion batteries (LIBs) offer an innovative solution for portable devices, they are also at increased risk for safety incursions. Flammable electrolyte, fast melting separators, and extra oxygen from specific cathodes can contribute to an already thermally or mechanically abused LIB, propagating a thermal runaway [1-2]. Researchers are investigating the contributions to thermal runaways and attempting to create safer practices or innovative materials and designs that can make these batteries safer, especially pertinent because as they often power devices near to humans. This research focuses on separator safety and examines the fire-retardant material, vermiculite, used as a modification layer on a common commercial separator material, polypropylene, to enhance the thermal stability of an LIB.

Most LIBs use electrochemically benign polymer-based separators, typically polypropylene (PP) and polyethylene (PE), to block the electrodes from contact [2]. While they have low resistance for ion transfer and are inexpensive and easy to manufacture, they can show shrinking characteristics as early as 130°C [3]. At ~160°C the PP separator vaporizes, thus the solid structure is absent which allows the electrodes to touch, thus insinuating a short-circuit. Separators that can withstand higher temperatures would delay potentially hazardous situations if the LIB were exposed to extreme temperatures.

Vermiculite, a clay that has been used in fire-proofing applications for decades, is an attractive material for suppressing LIB thermal runaways. Stable past 1000°C with impressive thermal properties, vermiculite has been incorporated into recent fire extinguisher technology to conceal and contain LIB fires. After vermiculite ore has been rapidly heated to 1000°C, the interlayer water (or hydroxyl water) molecules are released, and the structure expands axially [4]. This new product, expanded vermiculite, insulates well and suppresses flames. Depending upon where the vermiculite is mined, the molecular composition will vary. The general formula of vermiculite is represented as:

$X_4 (Y_{2-3}) O_{10} (OH)_2 M^{*n} H_2O$, where M is the exchangeable cations (Mg^{2+} , Ca^{2+} , Ba^{2+} , Na^+ , K^+), Y is the octahedral layer (Mg^{2+} , Fe^{2+} or Fe^{3+} , Al^{3+}), and X is the tetrahedral layer (Si, Al) [4]. The

vermiculite used in this research was taken from Palabora, South Africa, represented by the following half-unit cell formula:

$(\text{Si}_{3.02}\text{Al}_{0.79}\text{Ti}_{0.05}\text{Fe}^{3+}_{0.14})(\text{Mg}_{2.50}\text{Fe}^{2+}_{0.38}\text{Fe}^{3+}_{0.09})\text{O}_{10}(\text{OH},\text{F})_2\text{Ba}_{0.29}\text{K}_{0.14}\text{Ca}_{0.08}$ [4]. When ground into a powder and combined with a binder, a slurry can be casted, dried, and cut into separator size, ready to be assembled and tested in a battery.

After optimization of the application thickness and ratio, it was concluded that the addition of a vermiculite-PVdF modification increased the melting temperature by several degrees and decreased the amount of exothermic energy released during a heat ramp, alluding to a safer battery during thermal runaways.

2. LITERATURE REVIEW

Storing electricity for future use has been desirable for centuries. While the basic battery design is relatively consistent (electrodes, electrolyte, and structure), many components may be altered for different desired characteristics. These heavily researched components include the cathode and anode active material, the electrolyte, and the separator. The addition or substitution of different materials or chemical compounds can aid in the development of a more successful battery, whether it be lighter, smaller, more energy-dense, longer lasting, cheaper, or most importantly, safer. Unfortunately, these traits can be inversely related. For example, a material that gives high capacity may also show a short life span, or a high-energy dense material can also be heavy. Therefore, it is important to understand the goals of the specific application and optimize accordingly.

Lithium-ion battery work was first initiated by Nobel-Prize winners: Stanley Whittingham, John Goodenough, and Akira Yoshino, which was then commercialized in 1991 by Sony Inc. Accredited with an energy density almost five times higher than the then-popular zinc-mercury oxide, as well as a weight and volume decrease and operation life increase, lithium batteries became a popular topic of research around the world [5]. The reactivity of lithium and water gave rise to new electrolyte, and with it, new safety issues. This literature review examines the varieties in lithium batteries and common safety issues with a focus on separator safety.

During discharge, Li^+ ions flow from the negative anode electrode to the positive cathode electrode while the electrons travel in the outer circuit. The reverse is true during charging. The cathode materials must align with the following key requirements to enable success: readily reducible/oxidizable ions, reversible reactions with lithium (also with high free energy of reaction), rapid insertion and removal during reactions, good electronic conductor, stable, low cost, and environmentally benign [6]. Proposed by Goodenough in 1980, the lithium cobalt oxide (LCO) cathode has dominated the market for small-scale commercial applications [5-6]. Consequently, limited cobalt resources has continued to raise the price of this cathode. Although it maintains a smaller capacity, lithium manganese oxide (LMO) cathodes are less expensive and more abundant and less environmentally toxic than LCO cathodes [7]. The combination of LMO and LCO with the addition of nickel produces another common cathode: lithium nickel manganese cobalt oxide (NMC). This combination amalgamates both the positives and the negatives from the individual

cathodes. The shift towards nickel reduces the cost and increases the energy density and life span of the batteries [6]. Lithium iron phosphate (LFP) cathodes are inherently safer than LCO and LMO, due to the lack of flammable oxides. Their stability leads to a longer life span but tends to produce a lower specific energy than other cathodes [6].

Similarly, anode materials can be altered to a desired state while continuing to accomplish the key characteristics for an electrode. Lithium metal is a common anode used in lithium-ion batteries due to its high theoretical specific capacity [8]. Unfortunately, extensive cycling can produce lithium dendrite growth, enabling potential short circuits from separator penetration [6-7,9]. A shift to carbon anodes helped circumvent this issue, but at the cost of specific capacity as graphite can only exchange one lithium ion for every six carbon atoms [8]. Alternatively, silicon has been explored as anode material due to very high specific capacity. Unfortunately, large expansions and contractions (>300%) during cycling have kept this material from many commercial applications [8]. Other experimental anodes use a variety of new materials or the addition of chemical compounds to help mitigate these flaws [6-9].

Electrolyte is used to aid in the transfer of ions between the electrodes and may also be designed to achieve desired characteristics. After lithium had been introduced in batteries, the once aqueous electrolyte needed to shift to something more electrochemically stable. The solution was a combination of lithium salt and carbonate organic solvents, such as LiPF_6 in an ethylene carbonate/dimethyl carbonate solvent [5-6]. Consequently, when combined with a lithium anode, a reaction between the electrolyte and lithium can create uneven growth in a layer called the solid electrolyte interface (SEI) which can increase the potential for dendrite growth and ultimately, short-circuiting [5]. Solid-state batteries solve this issue. When combined with a ceramic or polymer, the solid electrolyte can act as separator and ion transport aid, mitigating issues from dendrite puncture [5-9]. The drawbacks of these electrolytes have made commercialization challenging. Achieving constant surface contact between the porous electrode and the solid electrolyte can be difficult, and solid electrolytes often exhibit lower ionic conductivity [8]. As with any battery component, it must be optimized to fit the specific needs of the goal.

To prevent electron flow inside the battery (short-circuit), the electrodes must be kept apart by an electrochemically benign porous separator that allows ion flow but prohibits electrode contact. Commercially, polymer separators have been employed due to durability, electrochemical stability, and decent wettability and ionic conductivity [10-12]. These separators (often

polyethylene, polypropylene, or composites of the two) exhibit a “shut-down” function at certain temperatures (~130°C) which close the pores and restrict further operation [13]. Past 160°C, these polymers shrink and no longer provide a barrier between the electrodes, driving researchers to develop more thermally stable separators, such as ceramic-based membranes [13]. Other reasons that new separator materials are researched is to hinder dendrite puncture, reduce cost, increase wettability and ionic conductivity, and to improve environmental friendliness. Separator modifications to pre-existing polymer separators compound the benefits of the polymer separator while providing additional advantages. For example, a thin ceramic coating on a polymer separator would remain intact past 160°C and restrict short-circuit until higher temperatures [3,14-15]. Unfortunately, lower ionic conductivities are often observed with ceramic-based separators due to pore blockage from particles [11-12]. Polymer separators will continue to dominate the market until a superior separator can be mass produced as easily and cost-effectively.

The previously mentioned short-circuits are instigated by a variety of stimuli and can produce quite hazardous events. Thermal runaway is the coined term for the propagation of exothermic reactions within a battery which can occur spontaneously above 80°C [1]. At elevated temperatures, SEI breakdown, electrode contact from separator shrinkage, and the exothermic reactions between the electrolyte and electrodes will create further temperature increase, insinuating pressure increase and ultimately, battery rupture [1-2]. Events such as external or internal (dendrite) penetration, extra stress/strain, cycling abuse, or operations at high temperatures can begin a thermal runaway. The flammable electrolyte and additional oxygen from specific cathodes can ignite and start a fire, further intensifying the incident [2]. Many researchers have delved into this broad topic to analyze and develop safer battery practices and/or more durable, thermally stable cathodes, anodes, electrolytes, and separators.

The discovery of the lithium battery brought international attention to the research of its components, as optimization was needed to ensure that specific needs were met. Many cathodes are used commercially, depending on their application, to include LCO, LFP, NMC, LFP, and others. For the opposing electrode, lithium metal, carbon, or silicon are popular. These materials have a variety of advantages and disadvantages, so it is important to pick the correct material for the right application. Electrolytes usually consist of a lithium salt in a carbonate organic solvent, but recent research has supported solid electrolytes for increased safety. Commercial separators are composed of polymer for durability and ease of manufacturing. The addition of materials, such

as ceramics, can increase characteristics like thermal stability, wettability, and ionic conductivity. When researching these battery components, safety is the most important aspect to consider. Thermal runaways are infamous in lithium batteries due to flammable electrolyte and additional oxygen from some cathodes. Mechanical, thermal, or electrical abuse can instigate a thermal runaway and lead to catastrophic incidents. Efforts must be taken to ensure safety when exploring a new material in a lithium battery.

3. MANUSCRIPT UNDER PREPARATION: FLAME RETARDANT VERMICULITE COATED ON POLYPROPYLENE SEPARATOR FOR LITHIUM-ION BATTERIES

This manuscript will be submitted to the Journal of Membrane Science for consideration.

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3.1 Abstract

Lithium-ion batteries (LIBs) are being used in a variety of applications due to their desirable energy storage characteristics required for modern electronic devices. However, LIBs are prone to thermal runaway due to flammable liquid electrolyte, decomposition of solid electrolyte interphase from anode surfaces, and melting of polypropylene (PP) separators. The separator provides a pathway for Li⁺ transfer and divides electrodes from electrical contact, avoiding a short circuit, a potentially catastrophic event. A separator that can endure higher temperatures may restrict a cell from causing thermal runaway. This paper demonstrates that vermiculite, a mineral stable over 1,000 °C, could act as a separator lining in LIBs with a lithium ion phosphate (LFP) cathode and lithium anode. Though the standard PP separator shrinks or melts above 130 °C, the vermiculite and binder will continue to provide electronic isolation, allowing the battery to delay a thermal runaway scenario. The vermiculite modified separator demonstrated less exothermic energy release during the thermal runaway, indicating enhanced safety in examined LIBs.

3.2 Introduction

Imagine a perfect battery: small, lightweight, affordable, powerful, and most importantly, ultra-safe. However, batteries that succeed in some of these traits will often fail in others. Introduced into the market in 1991, lithium-ion batteries (LIBs) have been targeted for further research and development due to their high capacity and lightweight charge supply abilities [1]. As these batteries grow in popularity, it is important to solve associated- ever-growing safety issues [1,2]. When an LIB is electrically, mechanically, or thermally abused, the follow-on events can be difficult to manage, leading to a phenomenon referred to as thermal runaway [3]. Short-circuiting due to electrode contact is a common catalyst for the thermal runaway that can ultimately result in damage to surrounding objects. Q. Wang *et al.* reported that the tens of thousands of mobile phone fires/explosions that have occurred since 2006 can be attributed to short circuit and overheating phenomena [3]. Within the battery assembly, the electrodes are typically isolated by a polymer separator. Once this material is exposed to temperatures above 130°C, shrinkage occurs, and the proceeding electrode contact produces a short-circuit [3-4]. This event causes rapid internal electron travel as well as reactions between the electrolyte and cathode that releases oxygen, resulting in a temperature and pressure increase. In such a scenario, if the separator could withstand hotter temperatures with minimal shrinkage, the thermal runaway could be delayed or even discontinued, mitigating catastrophic events [4].

In the field of internal thermal runaway mitigation in LIBs, research is divided into several categories. The design categories are: (1) smart batteries with internal sensors, meant to detect anomalies and report to the user for an active response [5-7], (2) certain material interactions that melt and provide a shut-down function, disabling operation [8-9], and (3) materials that can withstand hotter temperatures without degradation [10-11]. Alternatively, solid-state batteries can also provide an attractive solution to safety issues, combining the electrolyte and separator function into one, solid layer, allowing more properties to be altered to the desired state and ultimately increasing the operating temperature of the electrolyte and separator [12-13]. Since solid-state batteries still require more research before integration into larger applications, it is important to improve the thermal stability of current LIB designs.

Research literature also supports the modification of existing commercial separators to increase performance and/or enhance safety [14-15]. This method is desirable because the modifications can be combined with the benefits of pre-existing separators, such as low cost, manufacturing ease,

and high ionic conductivity. A common method of separator modification is incorporating a well-known fire-retardant material with a binder and casting it on a commercial separator [9,10,16]. Bayani *et al.* applied $\text{Al}(\text{OH})_3$ with a Poly(vinylidene Fluoride-co-hexafluoropropylene (PVDF-HFP)) binder onto polypropylene separators to enhance flame retardant properties [10]. Their modification also increased the wettability and ionic conductivity, although demonstrated capacity fade over time. Similarly, Yang *et al.* applied AlOOH and polyvinyl alcohol to polyethylene and observed interlocking structures at higher temperatures, acting at a shut-down function during hot operations [9]. It is commonly observed that a thicker modification layer will increase thermal properties at the cost of diminished electrochemical performance. Counterintuitively, Kannan *et al.* concluded that thicker (polyolefin) separator layers with less porosity may actually outperform their opposites due to the initial loss of lithium during SEI [17]. Therefore, thickness and porosity magnitude must be investigated to determine the optimal values for the specific modification being researched.

The goal of this research is to explore vermiculite: a common, inexpensive, lightweight, fire-retardant mineral with its use as a separator modifier. Vermiculite has been recently examined in lithium-sulfur (Li-S) batteries as both an anode (co-depositing lithium with a 2-D vermiculite shuttle) and separator to reduce shuttle effects [18-20], but not with lithium iron phosphate (LFP) cathodes to enhance thermal properties. While Li-S batteries can provide high specific energy, they usually exhibit a poor cycle life and efficiency and are therefore not used in a wide range of applications [21]. Therefore, this research focused on the success of vermiculite with LFP, a more widely applicable cathode. The binder used in this work was polyvinylidene fluoride (PVDF), a non-reactive specialty plastic commonly used in electrode fabrication due to comparatively high melting temperatures and extensive history and success in batteries. PVDF has also shown success in battery separator applications [12, 22-24] Ultimately, the vermiculite-PVDF modification improved the melting point by a few degrees and demonstrated lower exothermic energy release in calorimetric experiments. The modified separator also demonstrated comparable electrochemical performance, to include ionic conductivity and capacity during cycling.

3.3 Experimental Method

3.3.1 Procedure of vermiculite coating

A fire-retardant vermiculite additive, Polyvinylidene fluoride (PVdF) binder, and N-Methyl-2-pyrrolidone (NMP) solvent was homogenized. Specifically, expanded vermiculite from the Strong Company, Kynar HSV1800 from Arkema, and NMP from Sigma Aldrich were used. A mortar & pestle was used for five minutes to grind the vermiculite into micron-sized particles which were then sorted to sizes under 106 μm for several hours with sieves in a tap density machine. To prepare the slurry, the ratio of vermiculite to binder was 1:9 and the NMP solvent was added until the solution had a honey-like viscosity. Zirconia balls were also added to the mixture to assist with particle breakdown and the slurry was mixed for an accumulative 30 minutes in a Thinky centrifuge mixer. A doctor blade was used to cast the slurry 7 μm thick onto one side of polypropylene, specifically Celgard[®]-2500. These films were then dried in a vacuum oven at 80°C overnight and cut into 19 mm diameters circles, once cooled. Figure 1c shows this process. The modified separators were stored in the glovebox under conditions of 3.5 ppm O₂ and 0.5 ppm H₂O to minimize moisture and foreign particle containment.

Initially, when the vermiculite coating was in direct contact with the lithium anode, the battery could not charge, but when flipped to face the cathode, the battery could cycle. Therefore, the slurry was coated on one side of the PP and faced the LFP cathode. The difference between electrodes is the operating potentials. When the vermiculite faced the anode, operating between 0.01 – 1.5 V, the vermiculite exchanged its natural cations for lithium. In prior vermiculite separator research, the vermiculite was doped with lithium or sulfur (depending on the battery type) to pre-neutralize the separator and disable this behavior from occurring [18-19].

Ideally, a separator would not shrink or melt to delay or altogether stop a thermal runaway, all while remaining inert to the battery chemistry and providing smooth passage for the lithium ions. The initial design was a 7:3 ratio of vermiculite to PVdF applied onto the PP with a thickness of 27 μm . When heated on a hot plate, the separator did not display shrinkage past 500°C, as seen in figure 1S, but did not show favorable electrochemical performance. The thickness was decreased to 7 μm but continued to show capacity fade as seen in figure 2S. For the third and final iteration, the thickness was kept constant at 7 μm and the ratio was reversed to a 1:9 ratio of vermiculite to PVdF. The idea was to continue increasing the vermiculite from this ratio until thermal and

electrochemical performance was optimized, but this ratio was found to be optimized as the results showed comparable electrochemical performance as the pristine separator and it was recognized that additional vermiculite would only decrease the performance.

3.3.2 Fabrication of electrodes

The electrodes used in this research were lithium metal foil for the anode active material and lithium iron phosphate (MSE Supplies LLC) as the cathode active material. For cathode preparation, the binder was Kynar HSV1800, the conductive material was Super P from Timcal and the solvent was NMP, along with the LFP. The electrode slurry contained a ratio of 8:1:1 of active material, binder, and carbon, respectively. To aid in blending, zirconia balls were added. After thirty minutes in a Thinky centrifuge mixer, the slurry was cast on aluminum foil using a doctor blade set to 15 μm . Lastly, the films were dried in a vacuum oven at 80°C overnight, calendared to reduce the porosity, and then cut into 15.5 mm diameter circles for use in coin cells.

3.3.3 Coin cell assembly

The coin cells were assembled inside a glovebox under conditions of 3.5 ppm O₂ and 0.5 ppm H₂O. The schematic of the physical assembly for a LIB is displayed in Figure 1a. The cathode used in this research was LFP while the anode was lithium metal foil. During experimentation to test the vermiculite-coated polypropylene separator, the vermiculite film faced LFP. The electrodes and separators were cut at 15.5 mm and 19 mm, respectively, to ensure short-circuit safety. The electrolyte used in this research was 1M LiPF₆ in 1:1 EC:DEC. Two stainless steel spacers and one stainless steel spring were used to assist with proper structure and spacing. Once assembled, the cells were crimped at a pressure of 1000 psi.

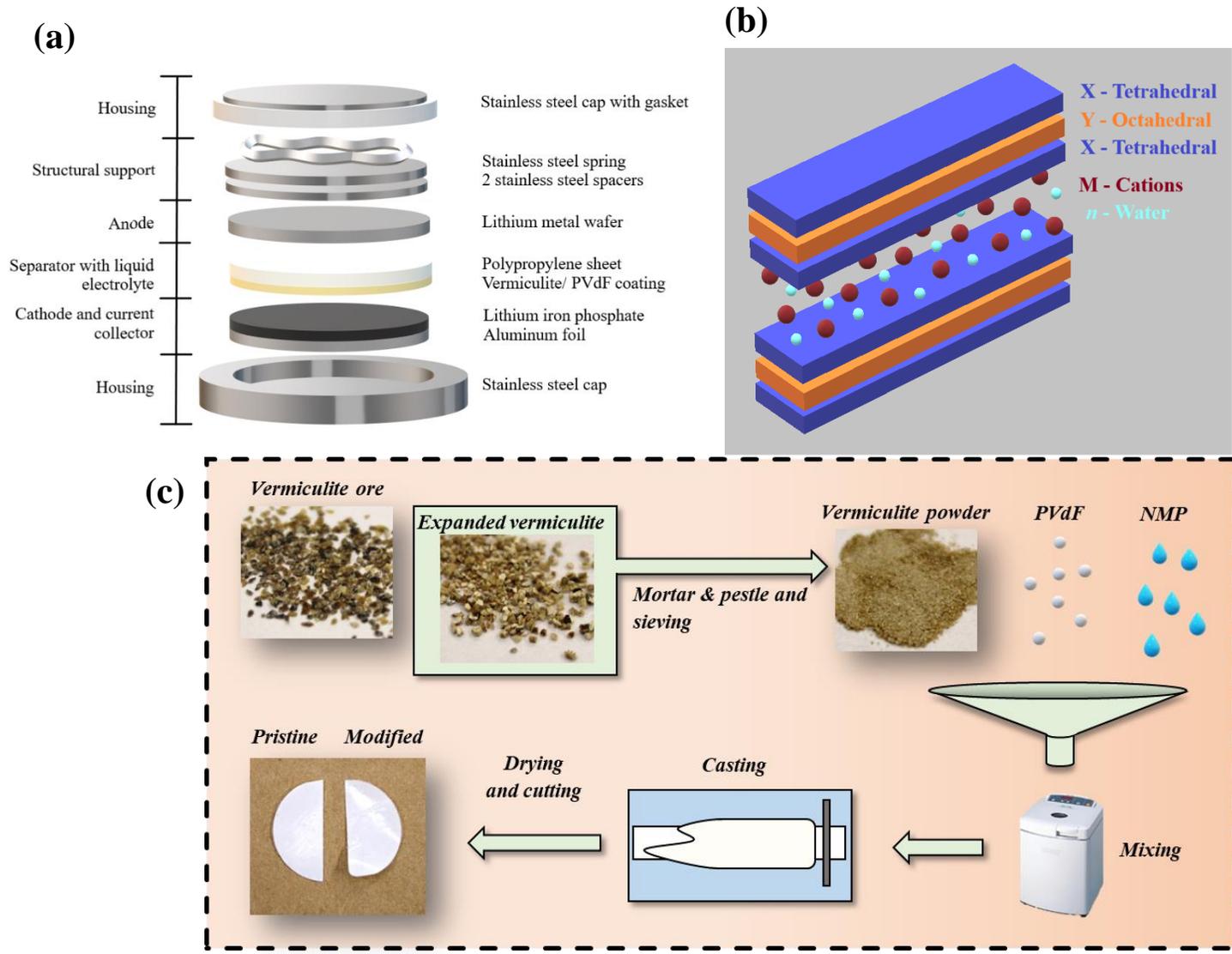


Figure 1. Schematics of (a) the half-cell coin battery assembly used in this research, (b) the basic clay structure of vermiculite, and (c) the procedure used to fabricate the vermiculite-PVdF modified separators.

3.3.4 Vermiculite characterization

Vermiculite is a 2:1 clay structure, with a tetrahedral layer located between two octahedral layers. The octahedral layer can be composed of either magnesium, aluminum, or iron, based on the surrounding materials from where it was mined [25-26]. The naturally occurring cations can be calcium, sodium, potassium, barium, or magnesium, but can exchange cations experimentally [25]. The tetrahedral layers in vermiculite are composed mostly of silicon with a small amount of aluminum. Figure 1b demonstrates the basic molecular model of vermiculite with the general half-unit cell as $X_4 (Y_{2-3}) O_{10} (OH)_2 M^*n H_2O$ [25]. When heated from its pristine, sheet-like form, released steam from the interlayer water causes the vermiculite to expand 10 to 20 times its original size [25]. Depending on where the vermiculite is mined, the interlayer water will be either water molecules or hydroxyl water, but the rapid heating has the same affect [25]. The vermiculite used for this research was mined from Palabora, South Africa and contains interlayer hydroxyl water. When obtained from the Strong Company, both the expanded and ore (pre-expanded) vermiculite particles were granular sized. The expanded particles were further ground in a mortar & pestle and then sieved in a tap density device to obtain particle sizes of 106 μm and smaller to enable thinner slurry layers. The differences in colors and structures of the vermiculite ore, expanded, and powder is shown in figure 1c. Literature gives the half-unit cell composition of Palabora vermiculite as: $(Si_{3.02}Al_{0.79}Ti_{0.05}Fe^{3+}_{0.14})(Mg_{2.50}Fe^{2+}_{0.38}Fe^{3+}_{0.09})O_{10}(OH,F)_2Ba_{0.29}K_{0.14}Ca_{0.08}$, defining the interlayer cations to be Ba, K, and Ca [25].

Several experiments were performed on the vermiculites to characterize their structure and chemical composition and better understand the molecular interactions when used inside batteries. Energy-dispersive X-ray spectroscopy (EDS), shown in figure 3S and table 1S, proposed potassium as the highest cation amount. The surface area of the pre-experimentally ground particles was also analyzed using Brunauer–Emmett–Teller (BET), shown in figure 4S. Here, the pore volume was observed to be $0.017 \text{ cm}^3 \text{ g}^{-1}$ with a surface area of $5.819 \text{ m}^2 \text{ g}^{-1}$. The ground vermiculite particles were subjected to Thermal Gravimetric Analysis (TGA), displayed in figure 6c as the green line, to characterize its thermal characteristics when heated. The modified separator was also exposed to the electrolyte to observe any potential reactions. When submerged for three days with a cover in the glovebox, there was no color change, alluding to the absence of any unwanted chemical reactions between the vermiculite and electrolyte.

An X-ray Diffraction (XRD) comparison showed structural difference between the pre-expanded and expanded vermiculite prior to experimental grinding, confirming crystal changes when the interlamellar water layers (in this case, hydroxyl water) are turned to steam and rapidly released during the expansion phase. This is demonstrated in figure 2. Balek *et al.* characterized vermiculite based on temperature and grinding size [27]. They discovered that the grinding decreased crystal size and increased crystal disorder, and that 10 minutes of grinding made the vermiculite amorphous. They also observed dehydration during temperature increase [27]. The research for this vermiculite coated separator did not focus on the structure change during the grinding stage and high-temperature experiments, therefore, further exploration into optimal grinding time for battery separator application may improve the results.

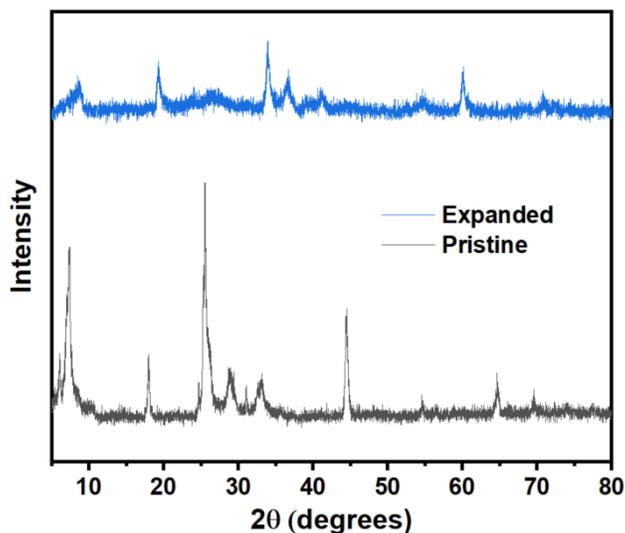


Figure 2. XRD pattern comparison for vermiculite ore and expanded vermiculite.

3.4 Results & Discussion

3.4.1 Physical characterization

It can be helpful to observe phenomena on a qualitative, micron level to better understand physical properties and relationships. Figure 3 portrays the separator design with attached SEM images for micron views of its different aspects. The geometrically symmetric fiber structure of the PP is demonstrated in figure 3a. The pores are easily visible and uniform in shape, although somewhat sporadic in their placement. Figure 3b shows the compact layer structure of vermiculite

before experimental micron grinding. Prior to obtaining the vermiculite, the large particles were processed into smaller sizes, hence the broken characteristic of the sheets. The modified layer is demonstrated in figure 3c. Although it contains fewer visible pores, the presence of nano-sized pores still exists which suffices for the small ions. The surface morphology also shows the uniform application of the coating as well as the smooth dispersion of the small vermiculite particles. Figure 3d displays the cross-section of the modified separator with a thickness of approximately 30 μm . The average thickness measurements of the modified separator ranged from 28 – 34 μm , with the pristine separator maintaining 25 μm . In figure 3d, the pristine PP layer is shown on the bottom, adhered to the carbon tape, with the vermiculite-PVdF modification layer on top. The boundary between the pristine and modified layers is adhered well, as the vermiculite-PVdF coating slightly percolated into the polypropylene.

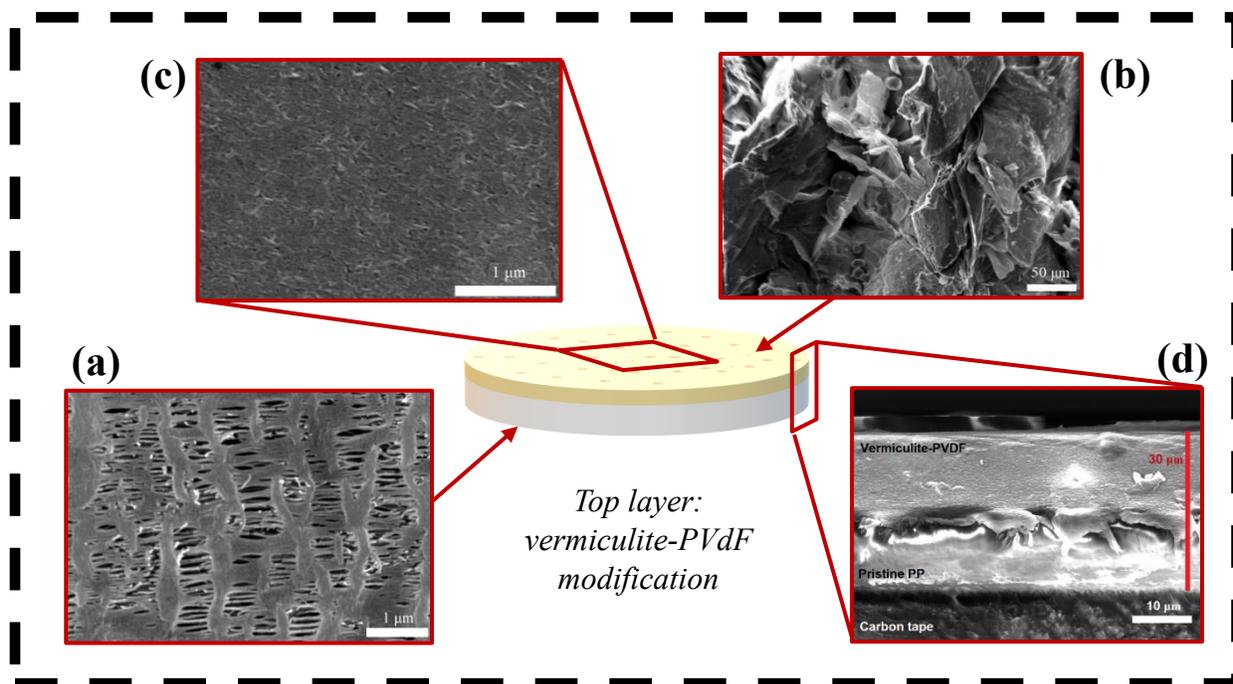


Figure 3. SEM images to show the (a) surface morphology of the pristine polypropylene, (b) the broken vermiculite sheets, (c) the vermiculite-PVdF coated polypropylene, and (d) the cross-section of the modified separator.

The cyclic voltammeteries (CVs) of the LFP cathode are compared for the 3rd cycle for cells comprised of pristine and modified separators as shown in figure 4a. The cells were cycled from 3.0 – 4.0 V at a scan rate of 0.2 mVs⁻¹. Similar profiles are expected due to the shared cathode,

LFP. The reduction and oxidation peaks of LFP for the cell comprising of the polypropylene separator are at 3.69 V and 3.22 V, respectively, whereas the reduction and oxidation peaks of LFP for the cell comprising of the modified separator are at 3.70 V and 3.23 V, respectively. The similar peak separation, ~ 0.47 V, for both cells implies similar electrode compatibility but the current peaks for the modified separator curve are sharper and more defined. This can indicate better electrode reaction kinetics and stability of separator without participating in the redox process [28].

Figure 4b displays electrochemical impedance spectroscopy (EIS) results. These measurements were taken immediately after cell assembly, preceding any cycling, as the electrolyte settled. In the high to medium frequency zone, the pristine separator cell begins at approximately zero and exhibits one semicircle, demonstrating the charge transfer resistance, $R_{\text{charge transfer}}$. The linear tail in the low frequency area denotes the lithium diffusion. The modified separator cell begins at 8.4 ohms. This gap (from zero ohms to the start of the data) is referred to as the bulk resistance, R_{bulk} , and includes the resistance of the electrodes, electrolyte, and separator [29]. As the cells contain the same cathode and anode, this resistance must be due to the modified layer on the separator. During the medium frequency stages, the modified separator exhibits two semicircles. The first displays resistance from the electrode-electrolyte interface [29], R_{CEI} , specifically the cathode electrolyte interface (CEI) because the assembly was a cathode half-cell. The appearance of this added resistance is due to the presence of the vermiculite layer facing the cathode, possibly participating the creation of the CEI and adding to the resistance through this interface. The second semicircle, portraying the charge transfer resistance, is slightly higher than the pristine separator cell, and the following tail exhibits slight restricted diffusion before becoming linear. While it is evident that the modified separator contributes to slightly higher resistance, it is still comparable to that of the pristine separator and does not negatively affect the cycling performance of the cell.

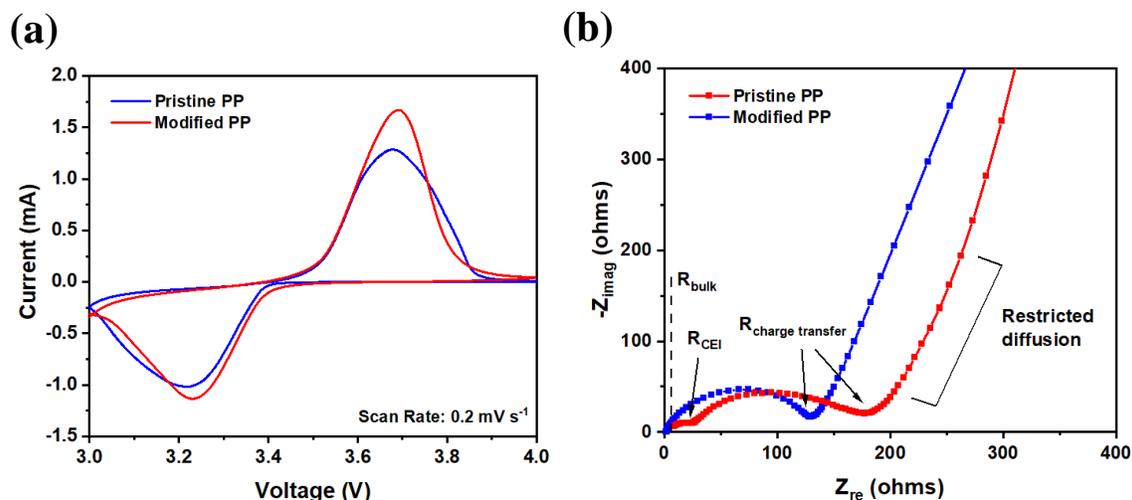


Figure 4. Characterization for separators: (a) cyclic voltammetry curve comparison of pristine and modified separator and (b) an initial EIS curve comparison for pristine and modified separators from $1e6 - 1e-2$ Hz.

3.4.2 Electrochemical performance

In order to be successful, a separator must provide smooth passage for the Li^+ ions, a structural block between electrodes, and be uninvolved in the battery chemistry, allowing the battery to operate with normal charge/discharge characteristics. To demonstrate successful cycling and capacity results, half-cells were assembled as depicted in figure 1a and cycled to show a variety of performance criteria. The voltage profiles for the pristine and modified separators are displayed in figures 5a and b, respectively. These graphs display the 3rd, 5th, 10th, 20th, and 30th cycle curves when cycled from 3.0—4.5 V at a constant current rate of 0.1C. The charge and discharge plateaus, ~3.46 V and 3.40 V, respectively, are similar for both pristine and modified separator cells, and consistent with 0.1C LFP plateaus in literature [30].

The theoretical capacity for LFP is 170 mAh g^{-1} with realistic capacities between $120 - 160 \text{ mAh g}^{-1}$, depending on the charge rate [31]. At a charge rate of 0.1C for an LFP cathode cell, charge-discharge capacities of $150/148 \text{ mAh g}^{-1}$, respectively, is to be expected [32]. We observed an initial discharge capacity of $\sim 148 \text{ mAh g}^{-1}$ for the pristine and modified separator cells, as seen in figure 5c. The modified PP cell maintained a comparable capacity to the pristine PP cell at cycle 35. At the 12th cycle, the modified separator cell exhibited a decline in Coulombic efficiency but ascended back to consistency by the 25th cycle. This behavior was observed in repeated

experiments and can be attributed to the vermiculite exchanging its original cations for the lithium, thus eliminating the lithium ions from participating in the capacity [33]. Exchanging the interlayer cations with lithium before assembly may reduce this behavior as performed by Xu *et al.* [19]. This would also enable the usage of a higher ratio of vermiculite, thus increasing the thermal stability, as seen from the hot plate tests in figure 1S when a ratio of 7:3 vermiculite to PVdF was used.

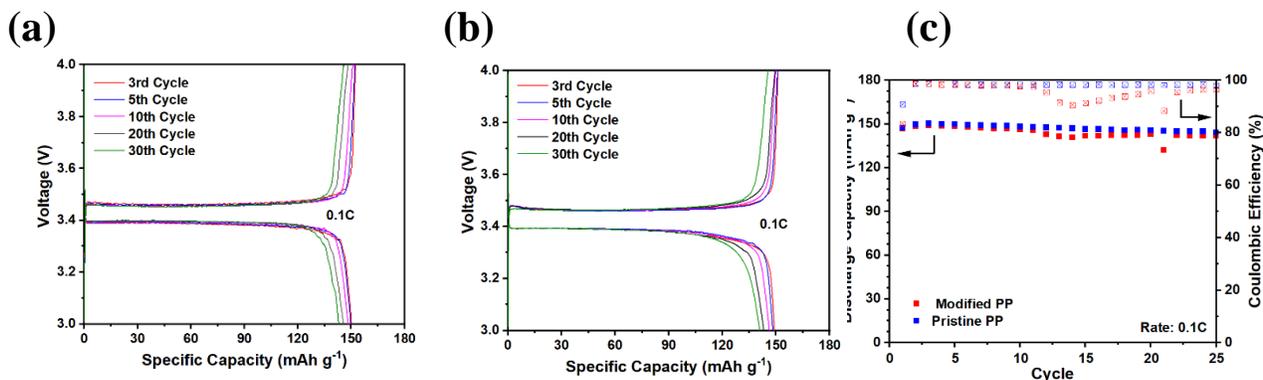


Figure 5. Electrochemical performance of LFP batteries to include (a) voltage profile for pristine polypropylene cell at 0.1C rate, (b) the voltage profile for the modified polypropylene separator cell at a 0.1C rate, and (c) a discharge curve and coulombic efficiency comparison at a 0.1C rate.

3.4.3 Thermal stability

When a battery experiences a temperature rise, the separator shrinks and creates an internal short circuit in the cell, causing self-propagation of a thermal runaway situation. To quantize this heat flux, cells and their components are exposed to temperatures in controlled experimental platforms such as multi-mode calorimetry (MMC) and differential scanning calorimetry (DSC). Thermal gravimetric analysis (TGA) is another tool that can provide quantitative information on the material before assembly. These results, such as the heat absorbed or released during the physiochemical processes, provide helpful information in characterizing the changes in the battery, such as determining the temperatures at which major events occur [34].

The pristine and modified separator were subjected to DSC testing to monitor differences in melting temperatures and enthalpies. Figure 6b displays the endothermic peaks and difference in characteristics. The modified separator had an ultimate melting temperature of 167.73°C, 3.38°C higher than the pristine separator. The integral of the normalized peaks for the pristine and modified separator was 101.7 J g⁻¹ and 83.16 J g⁻¹, respectively.

To accurately represent a thermal runaway situation, the separator must be exposed to heat in its assembled battery state as it is important to know parameters such as heat generation during the ongoing cycling processes. The presence of all the components of the battery helps prevent artifacts that can be generated from other analytical methods such as differential scanning calorimetry (DSC). Though DSC is used to study electrolyte salt decomposition, the reaction between electrolyte and electrode material, chemical reactions from SEI breakdown, and the thermal properties, the scale of the operation can create artifacts [34]. Thus, for the elucidation of the battery dynamics, more sophisticated characterization systems are required. MMC is the perfect union between accelerated rate calorimetry and DSC to measure specific heat phase change, chemical reactions, and run adiabatic processes. The cell efficiency for various chemistries can be measured to high accuracy from the heat flux obtained during cycling in MMC.

The cells in this test used a high-melting-point Teflon gasket to restrict the cell from opening up to the atmosphere during high temperatures. For the experiment, the cells were initially charged to 100% state of charge (SOC) and then heated in the vessel to 300°C at a rate of 0.5 K min⁻¹. Figure 6a displays the comparison for the pristine and modified separators. Both profiles exhibit a large endothermic peak around 178°C, signifying the melting of the PVdF and lithium anode. The following exothermic heat flux peak at 180°C for both cells indicates that the thermal runaway is due to the molten Li metal touching the cell case and producing an internal short circuit [12]. Other decompositions in the cells include the decomposition of the SEI from 80 – 120 °C and LFP and salt breakdown from 190 – 285 °C. The integral of the respective peaks divided by the weight of the active material in the battery is a helpful thermal characteristic used in identifying safety aspects in batteries. The exothermic areas between approximately 179 – 235°C were evaluated to be 0.953 kJ g⁻¹ for the modified separator cell and 2.628 kJ g⁻¹ for the pristine separator cell. The lesser energy released for the modified separator cell can be attributed to the modified layer continuing to provide some blockage between the electrodes, disabling a larger energy release. This equates to a safer battery as the energy dissipated to surrounding objects will have a less detrimental impact.

TGA was performed on each of the modified separator components, as well as their combined state, as shown in figure 6c, to observe mass degradation as the temperature was increased to 1000°C in an argon environment. The vermiculite showed the smallest weight decrease, losing only a few wt% total. Even after completion, the particles remained physically independent and

unchanged, proving a greater than 1000°C fusion point. The TGA of the modified separator was closest to that of polypropylene. Although the modified separator did not show superior results during the initial weight decrease, the curve flattens at a higher weight percentage than that of polypropylene. This remaining 8 wt% at 500°C is due to the vermiculite component in the coating, allowing the separator to remain partially intact during temperatures higher than 500°C. This is the expected amount since the slurry contains 10% vermiculite. The PVdF also contributed to the decreased rate of degradation in the modified separator as its decline occurred at a higher temperature and showed a slower rate of decline during its second phase at 490°C. These results suggest that the synergistic effect of each component in composite separator results in reduced exothermic heat released during thermal runaway reactions. It appears that the composite separator may be safer to use compared to the conventional pristine polypropylene separator for the advanced LIBs.

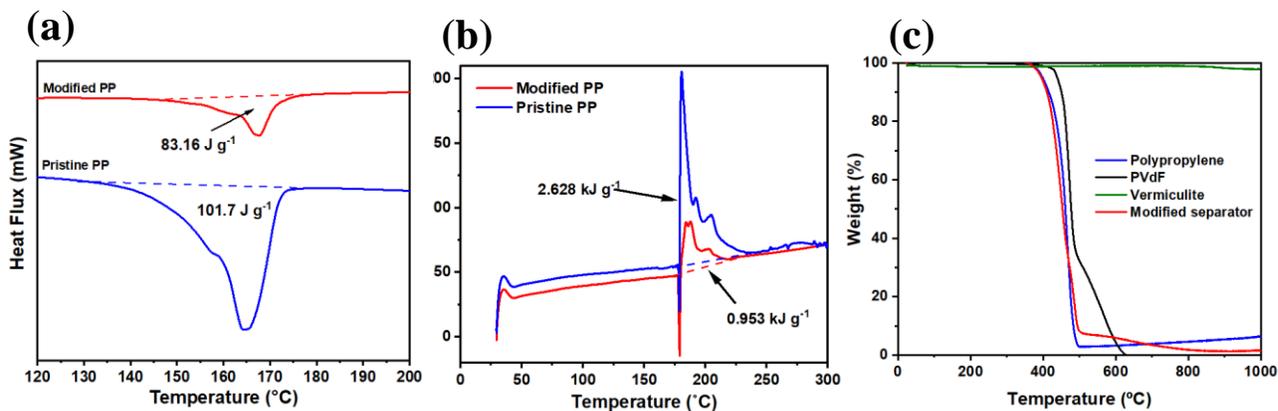


Figure 6. Thermal characteristic comparison between pristine and modified separator that includes (a) DSC analysis to 200°C at 5°C min⁻¹ under argon conditions, (b) MMC analysis to 300°C at a ramp rate of 5K min⁻¹, and (c) TGA comparison of polypropylene, PVdF, vermiculite, and the combined modified separator.

3.5 Conclusion

In this work, polypropylene separator surfaces in LFP cathode-based LIBs were modified by the addition of a 7 µm layer of 1:9 vermiculite and PVdF on one side of the polypropylene. It was observed that a thicker, more concentrated vermiculite layer resulted in high resistivity and fast capacity fade. The optimized separators were assembled with LFP cathodes vs. lithium and compared to pristine polypropylene separator batteries through a variety of thermal and

electrochemical performance tests. The electrochemical performance was comparable to the pristine PP, to include ionic conductivity and specific capacity. Calorimetry experiments showed less exothermic energy release and a slightly higher melting temperature for the vermiculite-PVdF modified PP. Ultimately, the addition of vermiculite onto the PP separator enhanced thermal safety without sacrificing electrochemical performance. Future work will focus on assembling the LFP cathode and proposed separator in LIBs for field testing.

3.6 Supplementary Material

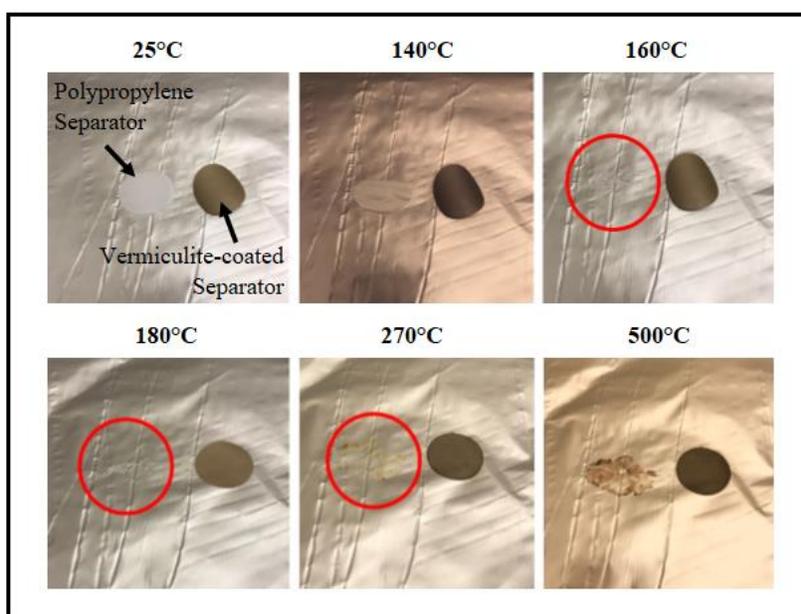


Figure 7S. Hot plate comparison results at temperatures of interest for pristine separator and modified separator with a 27 μm layer of a 7:3 ratio of vermiculite to PVdF.

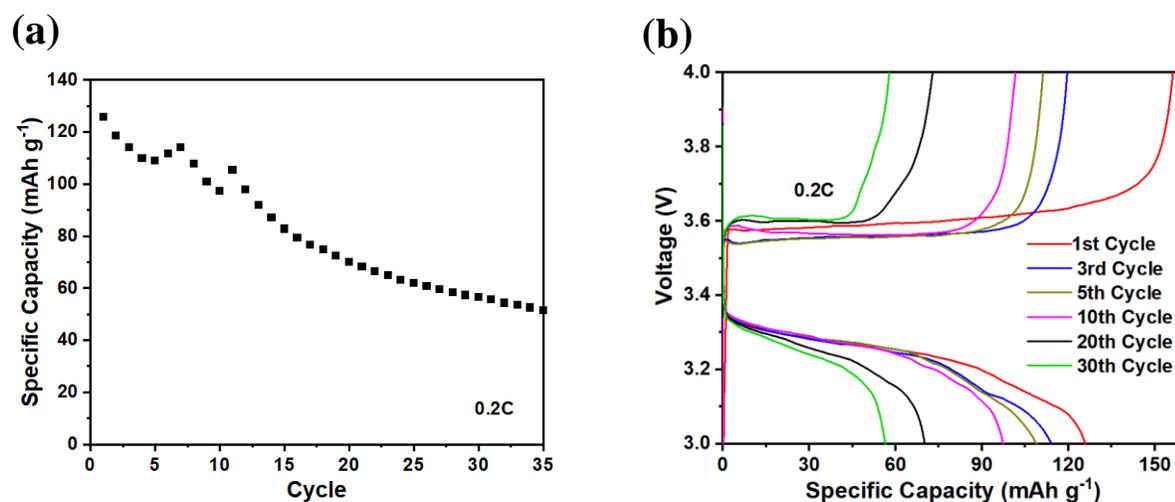


Figure 8S. Electrochemical performance of an LFP cathode with a modified separator of 7 μm thick slurry and 7:3 ratio of vermiculite to PVDF showing (a) the specific capacity at a 0.2C rate and (b) the voltage profile at a 0.2C.

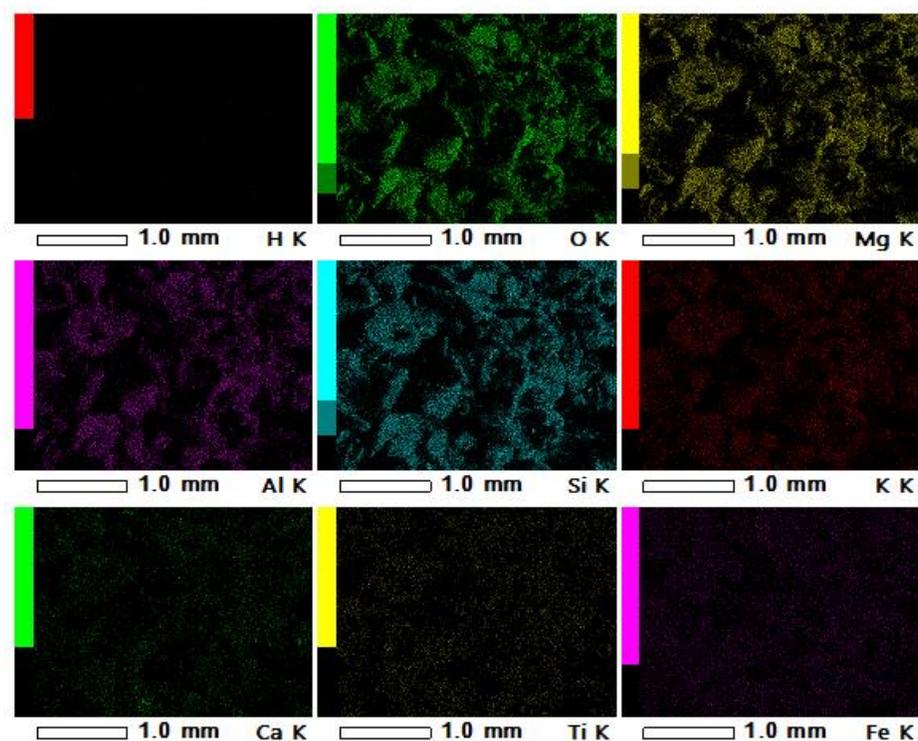


Figure 9S. Electron Diffraction Spectroscopy mapping the composition of expanded vermiculite prior to grinding at 512x384 resolution and 15 kV with a 0.2 msec dwell time.

Element	keV	Mass%	Sigma	Atom%	K
O	0.525	53.12	0.19	68.25	58.6083
Mg	1.253	13.95	0.08	11.80	9.9898
Al	1.486	4.28	0.05	3.26	3.0748
Si	1.739	14.75	0.08	10.80	12.6600
K	3.312	4.35	0.05	2.29	5.1809
Ca	3.690	0.39	0.03	0.20	0.4938
Ti	4.508	0.52	0.03	0.22	0.5683
Fe	6.398	8.64	0.11	3.18	9.4240

Table 1S. Corresponding table to figure 9S displaying the molecular details of the figure.

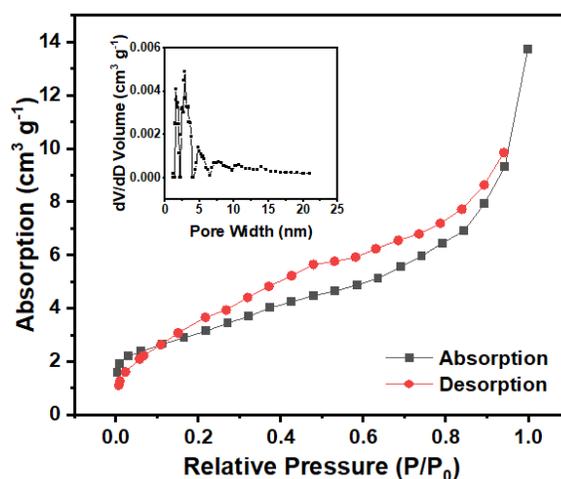


Figure 10S. BET of expanded vermiculite prior to grinding, degassed for 16 hours, with pore volume = $0.017 \text{ cm}^3 \text{ g}^{-1}$ and surface area = $5.819 \text{ m}^2 \text{ g}^{-1}$.

Equipment Specifications:

SEM: FEI NOVA nanoSEM Field Emission SEM

EDS: JCM-6000PLUS

TGA: Instrument Specialists TGA i1000 Thermogravimetric Analyzer

DSC: DSC Q20

MMC: Nexus MMC 274

EIS: Gamry Instruments Reference600 in a Gamry calibration shield

3.7 Acknowledgements

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3.8 Conflict of interest

The authors have no conflicts of interest to declare.

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4. CONCLUSION AND RECOMMENDATIONS

Although LIB have been available for a few decades, their safety remains an issue. Several components within the battery can drive a thermal runaway, presenting an extreme risk for surrounding objects. This research focused on separator safety by examining the application of a fire-retardant mineral, vermiculite, as a new LIB separator with a LFP cathode and lithium anode.

To ensure separator success, the film must be electrochemically benign, allow smooth ion transfer, and act as a block between the electrodes. Polypropylene (PP), a common commercial separator, accomplishes these key characteristics but fails to provide blockage beyond $\sim 130^{\circ}\text{C}$, when shrinkage starts to occur. If a LIB were exposed to high temperatures, the melted separator would enable electrode contact, allowing internal electron transfer, thus increasing temperature and pressure until a probable cell burst. Introducing a higher-melting temperature material to separators could delay or mitigate a potentially hazardous LIB thermal runaway.

Vermiculite was examined as a new separator material due to attractive thermal properties. With extensive fire-proofing history, this mineral can suppress flames and insulate against heat. The vermiculite was characterized through a variety of experiments, such as XRD, EDS, BET, and TGA, to understand its molecular composition and structure.

After grinding to a powder, the vermiculite was then combined with a binder, PVdF, into a slurry, and coated on PP. Optimization was needed to find a balance between electrochemical performance and thermal stability. The initial design used a 7:3 ratio of vermiculite to PVdF and was coated with a thickness of $27\ \mu\text{m}$. It was observed that the vermiculite disabled ion flow when faced toward the anode, therefore, future assemblies required placement of the layer toward the cathode. Electrochemical results for this design showed degraded capacity and low ionic conductivity, but demonstrated no shrinkage when exposed to a flame and heated on a hot plate to 500°C . While those thermal characteristics would be desirable for battery separator applications, the battery must show comparable cycling results to cells with PP separators. The modification layer thickness was reduced to $7\ \mu\text{m}$ but still demonstrated below average capacity and ionic conductivity. Once the ratio was reversed and the vermiculite portion deduced to 1:9 of vermiculite to PVdF, comparable electrochemical performance was achieved.

SEM was conducted on the ground vermiculite, pristine PP, modified separator surface, and the cross-section of the modified separator to characterize the surface morphology. The separators

were then assembled in batteries with LFP cathodes and lithium anodes and cycled. The initial capacity was the same as the pristine PP cells, ~148 mAh/g. The initial ionic conductivity (immediately after assembly) of the modified PP cell was observed to be higher than the pristine PP cell. The voltage profiles and cyclic voltammetry curves maintained similar plateaus and shapes.

Thermal stability experiments were also performed on the modified separators. DSC of the separator material as well as MMC of the separator assembled in a battery both demonstrated a lower exothermic energy release in the modified separator, proving that this modification would exhibit safer characteristics in the event of a thermal runaway.

There are a few recommendations that would improve future work on this research. Using fresh cathodes would help ensure maximum capacity results and eliminate false negatives in the data. Additionally, literature has shown that vermiculite has an affinity for exchanging cations. The low capacity results during the initial designs could be attributed to lithium loss during cation exchange in the vermiculite. If the vermiculite were doped with lithium prior to battery assembly, a larger capacity might be seen during cycling. This would enable a higher ratio of vermiculite, thus increasing the thermal stability and resulting in an even safer separator for LIBs.

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