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1. Executive Summary

The global demand for rechargeable batteries is large and growing rapidly. Assuming the adoption of electric vehicles continues to increase, the need for smaller, lighter, and less expensive batteries will become even more pressing. In this vein, PolyPlus Battery Company has developed ultra-light high performance batteries based on its proprietary protected lithium electrode (PLE) technology. The Company's Lithium-Air and Lithium-Seawater batteries have already demonstrated world record performance (verified by third party testing), and we are developing advanced lithium-sulfur batteries which have the potential deliver high performance at low cost. In this program PolyPlus Battery Company teamed with Corning Incorporated to transition the PLE technology from bench top fabrication using manual tooling to a pre-commercial semi-automated pilot line. At the inception of this program PolyPlus worked with a Tier 1 battery manufacturing engineering firm to design and build the first-of-its-kind pilot line for PLE production. The pilot line was shipped and installed in Berkeley, California several months after the start of the program. PolyPlus spent the next two years working with and optimizing the pilot line and now produces all of its PLEs on this line. The optimization process successfully increased the yield, throughput, and quality of PLEs produced on the pilot line. The Corning team focused on fabrication and scale-up of the ceramic membranes that are key to the PLE technology. PolyPlus next demonstrated that it could take Corning membranes through the pilot line process to produce state-of-the-art protected lithium electrodes. In the latter part of the program the Corning team developed alternative membranes targeted for the large rechargeable battery market. PolyPlus is now in discussions with several potential customers for its advanced PLE-enabled batteries, and is building relationships and infrastructure for the transition into manufacturing. It is likely that the next step will be accomplished through a combination of joint venture partnering and licensing of the technology.

2. Introduction

2.1 Technology: Batteries based on protected lithium electrodes

PolyPlus Battery Company develops lightweight batteries based on lithium metal anodes. In the early 2000s, PolyPlus invented and patented the protected lithium electrode (PLE), a core technology that enables the use of ultra-light metallic lithium anodes in batteries. PolyPlus has used the PLE concept to develop both primary and rechargeable batteries with unprecedented energy densities.

PolyPlus' inventions include non-aqueous Li/sulfur batteries, primary Li-Seawater, primary and rechargeable Li-Air, and rechargeable aqueous Li-Sulfur batteries. The energy density of these battery technologies is two to ten times higher than the competition including magnesium-seawater batteries, conventional primary lithium batteries, and rechargeable Li-ion batteries for consumer, industrial, and electric vehicle applications. PolyPlus has already demonstrated primary Li-air and Li-water batteries with record-setting specific energies of 800 Wh/kg and 1300 Wh/kg, respectively. PolyPlus is concurrently developing PLE- enabled rechargeable Li-sulfur batteries with projected performances of 650 Wh/l and 400 Wh/kg. These transformational technologies promise wide-ranging economic, environmental and energy benefits assuming successful development, scaling, and commercialization.

2.2 Goal: Demonstrating scalability

The key barrier to widespread adoption of battery systems for energy storage in electric vehicles and for the electric grid is cost. The path to significant battery cost reduction and U.S. competitiveness will almost certainly rely on the commercial introduction of domestically manufactured, step-change battery technologies. To realize the significant cost reductions possible with PLE-enabled batteries, it is critical to demonstrate scalability of both membrane production and the battery structures.

Accordingly, the focus of PolyPlus and Corning's Innovative Manufacturing Initiative (IMI) program included scale-up from bench-scale to a pilot-scale manufacturing processes, ultimately demonstrating the capability to make hundreds of solid electrolyte pieces per day at high yield. The entire manufacturing process was addressed, including raw material selection, powder preparation, tape-casting and sintering, and final part finishing and handling. The PolyPlus IMI effort also covered optimization and pilot production of the protected lithium electrode (PLE) and demonstration of high cycling efficiency for the lithium electrode. PolyPlus worked with team member Corning Incorporated to develop new techniques for producing the solid electrolyte membranes used in the PLEs, and to improve the conductivity of the solid electrolyte membrane to achieve higher energy and power densities in finished batteries. The mechanical properties of the ceramic membranes were evaluated in the laboratory and on the PLE pilot line, leading ultimately to optimization of the pilot process, and constructive feedback to Corning on their membrane fabrication process. PLEs produced on the pilot line were electrochemically evaluated in terms of rate capability, cycling efficiency, and failure modes.

2.3 Application and impact

Advanced PolyPlus batteries offer the promise of cost reductions in excess of 50% at the cell level relative to competing technologies, assuming that scaling the technology follows a similar trajectory as for conventional batteries. Introduction of the lower-cost, high energy density Li-air and Li-sulfur technologies developed in this Advanced Manufacturing Initiative program will facilitate vast improvements in energy utilization as it pertains to the Light-Duty Vehicle (LDV) fleet and, simultaneously, shift use patterns away from petroleum based fuels by displacing conventional internal combustion engine (ICE) vehicles over time. For instance, assuming an LDV fleet of 200 million units and a battery electric vehicle (BEV)/ plug-in hybrid electric vehicle (PHEV) market share of 2% and 5% by 2020 and 2030 respectively, an annual energy savings of about 100 trillion Btus (in 2020) and 250 trillion Btus (in 2030) can be achieved, based on improved well-to-wheel energy efficiency of PHEVs/BEVs relative to that of ICE vehicles [1,2]. Moreover, displacing ICE vehicles with EVs would reduce petroleum usage, which, based on the above 2030 scenario, could lead to a petroleum energy savings of more than 500 trillion Btus per year. If further cost reductions in solid electrolyte membrane pricing and PLE manufacturing are realized, Li-air and Li-sulfur batteries could also be compelling for grid energy storage to compensate for increased use of renewables, leading to further reductions in greenhouse gases.

2.4 Commercialization

The market potential for the technologies developed here is enormous. Rechargeable Li-air and

Li-sulfur batteries address markets that are valued in the tens of billions of dollars and growing. Additionally, PolyPlus has already demonstrated primary Li-air and Li-water battery prototypes with unprecedented energy densities, as mentioned above, and the cost of raw materials for these battery systems are lower than for competing chemistries. PolyPlus has been approached by a number of customers for these compelling primary batteries, which are also environmentally friendly and safe. The Li-water batteries are enabling for applications ranging from oceanographic exploration to powering autonomous underwater vehicles (UUVs), sensors, and buoys for the U.S. Navy. Product rollout is expected to start with primary Li-water batteries, followed by the introduction of ultra-lightweight Li-air primary batteries for the U.S. Army, and possibly for the growing unmanned aerial vehicles (UAV) market. The commercial availability of ultra-lightweight and compact batteries based on PLE technology will be enabling for a new generation of portable devices, resulting in economic benefits beyond those that can be delimited today. PolyPlus has met with large companies interested in higher energy, lighter weight batteries for current and future consumer electronics products. Since the novel manufacturing technology required to build and deploy these advanced battery systems was developed here - for the first time - the economic result of the successful program completion will create construction, engineering, manufacturing, and sales jobs that will be part of the manufacturing infrastructure for effective scaling and commercialization of the emerging technologies.

3. Background

3.1 State of the Art

The Li-ion battery is the current state-of-the-art for rechargeable battery technology. Commercialized by Sony in 1990, Li-ion battery technology has transformed the consumer electronics industry over the past 25 years. However, the Li-ion technology is reaching its limits, and dramatic improvements in rechargeable battery technology are still needed to enable widespread adoption of electric vehicles, and to support the increased and efficient use of renewables on the electric grid. One such advance would be the commercial introduction of rechargeable batteries based on lithium metal negative electrodes. This has eluded battery researchers across the globe for decades due to the difficulty in stripping and plating lithium efficiently, dendrite growth during cell charge, and associated safety issues.

The invention and engineering of protected lithium electrodes (PLEs) by PolyPlus Battery Company enabled a new generation of ultra-high energy density batteries, including lithium-air, lithium-water, and lithium-sulfur technologies. The water-stable PLE has been broadly recognized for its originality and innovative impact [3]. **TIME** magazine recently chose the invention of the PLE by PolyPlus as one of the 50 Best Inventions of 2011 and highlighted the technology in the November 28th issue [4]. Steve Visco, the CEO and CTO of PolyPlus was also selected for the 2011 International Battery Association Award for “Outstanding Contributions to the Development of Lithium-Air and Lithium-Water Batteries.”

PolyPlus has built 13 Ah lithium-water batteries with a demonstrated specific energy of more than 1300 Wh/kg, the highest ever achieved for any battery chemistry. PolyPlus has also developed fully engineered 10 Ah lithium-air cells that have achieved a specific energy of 800 Wh/kg. PolyPlus researchers are the first to demonstrate the reversibility of the aqueous lithium-air couple, and have made rapid progress towards the development of rechargeable lithium-air batteries. Isolation of the lithium metal electrode from the cathode chemistry is enabling for the development of lithium-air and lithium-water batteries, as well as for lithium- sulfur technology where corrosion of the lithium electrode by soluble polysulfide species is life-limiting. PolyPlus has demonstrated remarkable stability of the PLE in a variety of aqueous electrolytes including those developed for primary and secondary lithium-air batteries and even in seawater (which has a high concentration of Na^+ ions). The PLE is based on the use of LISICON ceramic membranes (NASICON crystal structure) with a stoichiometry described by $Li_{1+x+y}(M, Al, Ga)_x(Ge_{1-q}Ti_q)_{2-x}Si_yP_{3-y}O_{12}$ where $0<r\leq1$, $0<y\leq1$, and $0<q\leq1$, and where M is an element selected from the group consisting of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb [5-8]. The Li^+ conductivity ranges between a low of 10^{-4} S/cm to a maximum of 10^{-3} S/cm depending on composition and processing.

PolyPlus has built a comprehensive intellectual property portfolio covering most if not all aspects of the protected lithium electrode and the batteries it enables. The technology covers a diverse array of applications ranging from lithium-air, lithium-water, and lithium-sulfur batteries, to drug delivery (bipolar disorder), implantable power sources, and the recycling of lithium from waste streams (electroplating of lithium metal from aqueous solutions). This will allow PolyPlus to control access, and command premium margins on its technology.

In this program, PolyPlus has teamed with Corning, Inc. to demonstrate the manufacturability of PLE technology. The focus of this advanced manufacturing development program is to produce high performance PLEs using novel, scalable manufacturing processes. The PLE-based batteries, completely owned and independently developed by PolyPlus, are fundamentally different from all existing Li-ion and other battery systems. Similarly, the manufacturing technologies are being demonstrated and developed for the first time. Prior to this program, PolyPlus had about 10 years experience assembling PLEs and enabled batteries by hand on its manual line. During that time, iterative improvements to the process were developed and enacted. At the start of this program (Oct. 2012), the first-of-its-kind pilot PLE manufacturing line was in the process of being designed and assembled by the equipment manufacturer with feedback from PolyPlus. In the second program quarter (Feb. 2013) the equipment was shipped and installed at PolyPlus. Optimization of the semi-automated manufacturing line was the next task. The PLE manufacturing includes many difficult, integrated steps, including the handling, sealing, and assembly of thin ceramic plates and other fragile or volatile components. Manufacturing deficiencies were identified, with fixes subsequently designed and implemented. Such deficiencies are expected in any first-of-its-kind construction, and PolyPlus worked to design the necessary solutions for all encountered issues. At the end of the program (Sept. 2015), the pilot line was fully operational and capable of producing PLEs at high yield at the rated capacity.

A significant component of the program was developing the Li-conductive ceramic membranes, using a process that allows for high quality material properties and scalable, economically viable manufacturing. Commercial applications targeted by PolyPlus (including sonobuoys, portable solider power packs, and advanced rechargeable systems) demand high baseline conductivities and thin plates. In this program, Corning was tasked with developing thin, high conductivity ceramic plates for use in the PolyPlus PLE and related batteries. For successful commercialization, these plates needed to be pinhole-free, chemically stable in the operating conditions (Li-water, Li-air, and Li-S environments) and mechanically stable to survive the pilot assembly process and heat sealing. Corning developed a process to produce this product using ceramic processing techniques that are scalable and economically promising.

After demonstrating manufacturability of the PLE technology on its pilot line, PolyPlus intends to spend one year on market development, followed by commercial introduction of the lithium-water battery in approximately 24 months. Early introduction of its lithium-water battery technology will provide revenue, and market feedback to facilitate development of PLEs for secondary lithium-air and lithium-sulfur batteries. The step-change nature of these battery technologies should allow U.S. battery companies to maintain competitive margins on its product line, and pave the way for scale-up and exports to overseas markets. PolyPlus will grow based on revenues from sales of PLEs, lithium-water, lithium-air, and possibly lithium-sulfur batteries, as well as from royalties payed on gross sales from licensed battery manufacturers. At the conclusion of the proposed effort, PolyPlus and Corning will be poised to transition the technology to high-volume manufacturing.

3.3 Project Team

PolyPlus is the global leader in protected electrode technology, and in teaming with Corning Incorporated, the companies have all the requisite talent to develop a world-class product.

3.3.1 PolyPlus Battery Company

Since its incorporation in 1991, PolyPlus Battery Company has done pioneering work in the lithium battery field including the development of advanced lithium-sulfur battery technology (now licensed as a commercial product), the invention of the protected lithium electrode (PLE), and the battery chemistries enable by the PLE including primary and secondary Li-Air and Li-Water technologies. PolyPlus currently employs a team of 7 PhDs, 3 mechanical engineers, several chemical engineers and chemists, and associated support staff. The full PolyPlus staff has expertise in materials science, solid-state ionics, fuel cells, electrochemistry, lithium batteries, and characterization techniques. PolyPlus has generated 137 issued patents (U.S. and Foreign) and has 40 patents pending. The company has the internal capability to carry out fundamental investigations of electrochemical systems, and has the engineering talent to design and build cell hardware and battery prototypes.

3.3.2 Corning Inc.

Corning is a world leader in specialty glass and ceramics and has a proven track record of moving technology from the laboratory to the marketplace. Historically, Corning pioneered the development and introduction of a number of key industrial markets, leveraging expertise in materials and associated process development. Corning's contribution to the automotive emissions control market is an enduring example of this capability. With the first major Clean Air Act and creation of the Environmental Protection Agency in 1970, strong motor vehicle emissions reductions were introduced for vehicles to be produced in the 1975 model year. At the time, a solution meeting automakers' performance and cost requirements did not exist, and Corning was urged to work on the problem. Corning scientists began exploring cellular ceramic monoliths as a potential material that could survive the high temperatures and caustic environment of a catalytic converter system, and within a year the first prototypes were extruded in Corning's R&D facility. In 1972, Corning scientists further refined the technology by introducing low expansion cordierite ceramic compositions capable of withstanding high temperature and significant thermal shock. Corning committed to the pending market in 1973, breaking ground on a full-scale manufacturing facility, with commercial shipments beginning in 1974. By 1975, 3 million ceramic substrates were sold into vehicles produced for the US market. Today, virtually every automotive company in the world relies on the basis of the Corning team's cellular ceramic technology to control exhaust emissions. Millions of Corning ceramic "honeycomb" monoliths are extruded with tight dimensional and mechanical requirements, supporting a business with annual sales exceeding 800 million USD. Similar examples of Corning responding to demanding industry requirements in the liquid crystal display and optical fiber industries further emphasize Corning's expertise in materials and process development, taking concepts from lab scale research to high volume manufacturing.

4. Results and Discussion

4.1 Summary of Technical Approach

The goal of this IMI program was for the PolyPlus/Corning team to develop and demonstrate the manufacturability of PLE technology for the first time. The program's technical approach involved three main tasks, which were executed sequentially, competing one task per year of the program. A fourth task, the benefits assessment, was conducted at the beginning and end of the project. The tasks were defined as follows:

4.1.1 Task 1 - Membrane Development, PLE Development, and Manufacturing Assessment:

The "Membrane Development" portion of Task 1 focused on performance and manufacturability of the solid electrolyte membranes. To define the performance needs, PolyPlus worked with potential customers of the Li-water, Li-air, and Li-sulfur batteries to define detailed system requirements for target applications, including specifications for the ceramic membrane component of the batteries. To prove manufacturability of the membranes, Corning defined ceramics processing steps that would yield membranes with appropriate strength, chemical stability, and conductivity, while remaining amenable to high throughput manufacturing.

The "PLE development" portion of Task 1 focused on the design, build, installation, and shakedown and troubleshooting of the first pilot line for building PLEs. In this task, PolyPlus reviewed the completed design drawings, flew to the manufacturer to conduct an on-site evaluation of the line, and approved the line for shipping to Berkeley. The pilot line was installed and operational by the end of the second quarter of the first budget period. PolyPlus evaluated PLEs built on the pilot line in terms of Li^+ conductivity, and electrochemical and chemical stability in the various cell chemistries: Li-water, Li-air, and Li-sulfur. PolyPlus fully characterized the membranes and communicated the results back to Corning to facilitate their modification and further development of the membranes.

The final portion of Task 1 was a manufacturing assessment in which PolyPlus and Corning conducted a preliminary study on the manufacturing requirements for high volume secondary battery, specifically rechargeable lithium-sulfur batteries. This task focused on establishing joint technology, cost, and quality requirements for high volume battery production for mass-market applications. PolyPlus established a PLE performance baseline by applying standard battery testing procedures. Based on these initial test results, PolyPlus and Corning defined performance and quality test protocols for the PLE technology scale-up.

4.1.2 Task 2 – Process Development: Membrane process refinement, Mechanical and electrochemical testing, and Manufacturing enablement

To refine the membrane manufacturing process, Corning worked to optimize the solid electrolyte membranes for the individual battery types. Corning explored bulk membrane compositions as well as surface treatments to satisfy target application requirements. Meanwhile, PolyPlus worked with potential customers to define the specifications for the membrane and PLE for the first commercial product, and preliminary specifications for the later products.

To verify the performance of the LATP membranes produced by Corning, PolyPlus carried out mechanical and electrochemical testing, and compared the results to the membranes from our Japanese supplier. Membranes were fully characterized to relevant requirements and failure analysis was performed to guide membrane refinement tasks. Relevant tests included long term chemical stability testing, conductivity measurements, mechanical impact/shock, thermal shock, mechanical load induced under cycling and four-point bending. In addition, PolyPlus used the PLEs produced on the pilot line in Li-water, Li-air, and Li-sulfur batteries, tested their electrochemical performance, and fed back the data to Corning for further optimization of the solid electrolyte membranes, while optimizing the other constituents such as the multi-layer laminates and seals. The team established initial Quality Assurance guidelines for the membranes and PLE production. Finally, to develop best practices for manufacturing, PolyPlus reviewed the pilot line design and setup to ensure high process efficiency, safety, and applicability of scale-up process learnings in a competitive industrial manufacturing environment.

At the end of these first two portions of Task 2, PolyPlus met all milestones and completed all go/no-go criteria for the budget periods. The PLEs produced on the pilot line performed better than those assembled using hand tools, and with excellent repeatability of the mechanical and electrochemical performance. Also at this juncture, Corning made some changes to its scope of work. Considering that the electric vehicle market has the highest market potential, and Corning's belief that a high performance electric vehicle battery based on PolyPlus Li-sulfur chemistry would require uniquely differentiated attributes, Corning decided to narrow the scope of solid electrolyte effort to focus solely on materials that support secondary Li-sulfur designs. Corning's milestones for Task 3 were revised to focus on the development of a ceramic membrane with the garnet composition (LLZO) - a material that is earlier stage than the LATP composition but that promised better stability and conductivity.

4.1.3 Task 3 - Commercial Line Development: Process scalability and Path to manufacturing

To demonstrate process scalability, Corning conducted a feasibility (paper) study to ensure the production capability of thousands of membranes per day, which is necessary for commercialization. In addition, Corning outlined a timeline to manufacturing appropriate for anticipated commercialization of the first product. PolyPlus performed mechanical and electrochemical tests on the garnet pellets provided by Corning to ensure that they met the performance specifications. The garnet membranes showed good stability to lithium metal contact, but poor stability to lithium metal cycling.

To demonstrate the path to manufacturing, PolyPlus produced 2” x 2” based PLEs on the pilot line for its advanced batteries. PolyPlus carried out electrochemical testing of the 2” x 2” PLEs in Li-water, Li-air, and rechargeable Li-sulfur cells. PolyPlus demonstrated that the piloted PLEs hit commercial targets for Li-water and Li-Air customers, and hit pre-commercial goals for rechargeable Li-sulfur cells.

Concurrent with the above Task 3 items, the team specified Li-air and Li-sulfur membrane and cell technology for secondary automotive battery applications, provided feedback and testing for Li-sulfur cell scale up, and indicated which products are ready to be transitioned to the commercial marketplace.

At the close of the project, the following final goals were met:

G 3.1 Pilot was line operational at a rated output of five 2” x 2” (~10 Ah) PLEs per hour. Corning demonstrated the ability to tape cast garnet solid electrolyte membranes, 1x1 inch in size, 200 microns in thickness. Demonstration consisted of 4 parts that met these requirements and were hermetic.

G 3.2 PolyPlus provided electrochemical test data for ten 10 Ah PLEs produced on the pilot line demonstrating full utilization of lithium in the PLEs (>90%).

4.1.4 Task 4 - Market, Environmental, and Energy Benefit Analysis

The project team estimated the potential economic benefits ($/year), environmental benefits (reduction in CO_2 emissions, Mlb/yr, other) and market benefits (US economy) that can be realized in year 2020, assuming successful development and commercialization of the technology being developed. See the Benefits Assessment section for details. The potential benefits of the technology were calculated at the front end of the project and were reported in the first quarterly report. The market assessment was updated and submitted with the continuation applications submitted at each budget period end date. Towards the end of the project, the potential benefits were be recalculated to reflect the impact of the results of the project. The final report includes the final assessment and a discussion on the differences between the initial and final assessment.

4.2 Summary of Results

The results of this Department of Energy - Innovative Manufacturing Initiative program with PolyPlus Battery Company and Corning are as follows:

1. For the first time, a semi-automated pilot line for the production of protected lithium electrodes (PLEs) has been conceived, built, and installed in Berkeley, CA, and is fully

operational, with the ability to produce five 10-Ah PLEs per hour at high yield. The performance of PLEs produced on this line is high quality and repeatable. PolyPlus currently utilizes the PLEs produced on the pilot line in its three battery types, and all three types have achieved the commercial and pre-commercial battery performance specifications defined by potential customers.

2. Corning, Inc. worked closely with PolyPlus to determine the specifications for the ceramic membranes. Corning developed a method of producing membranes via tape casting that yielded a membrane with the LATP composition that survived for hundreds of cycles in PolyPlus' rechargeable Li-S lab cell. Feedback from PolyPlus on the performance of the membranes was incorporated into Corning's ceramics process. Corning also provided several ceramic pellet samples with the garnet composition that were stable to contact with lithium metal, although they failed upon cycling. Finally, Corning's feasibility study for membrane production showed that for high volume markets, membranes can be produced at low enough cost to reach the aggressive electric vehicle cost targets.

3. The combination of the above results is significant because it represents the successful first step toward the transition to manufacturing and scale-up of PolyPlus' advanced lithium metal batteries.

5. Benefits Assessment

PolyPlus Battery Company is working to develop the manufacturing technology to produce advanced protected lithium electrodes (PLEs) for PolyPlus' Li-air, Li-water, and Li-sulfur battery technologies. These transformational technologies promise wide-ranging economic, environmental and energy benefits assuming successful development, scaling, and commercialization.

The step-change improvement in energy densities provided by the rechargeable PLE-enabled batteries, coupled with the drastic potential cost reduction, will provide the basis for insertion of the technologies into the important future electric vehicle (xEV) and, potentially, the grid storage markets. Currently, the key barrier to widespread adoption of battery systems for energy storage for xEVs and the grid is cost. Although the price of lithium-ion batteries has decreased with manufacturing volume since its commercial introduction in the early 1990's, EV battery pack costs are still far too high to facilitate mass adoption of electrified transportation. Unless the price of oil increases well above that projected by energy analysts and/or the price of Li-ion batteries are substantially reduced, it is highly unlikely that electric vehicles can compete on price with conventional vehicles in the foreseeable future. Moreover, manufacturers of Li-ion batteries in the U.S. are faced with an extremely competitive global landscape in which margins on battery sales are razor thin. The path to significant battery cost reduction and U.S. competitiveness will almost certainly rely on the commercial introduction of a domestically manufactured step-change battery technology.

The economic benefit of driving an electric vehicle can be pronounced for the consumer when comparing the cost of driving using electric "fuel" as opposed to gasoline. This is illustrated in a DOE website that compares the cost of a gallon of gasoline to an "eGallon." [9] Data is provided for both national averages as well as each state, and is updated regularly. At the current time

(September 2015), fueling costs for the US average consumer are approximately half the cost when driving an EV as opposed to a standard gasoline vehicle. Due to changes in electricity and fuel costs over the past three years, the advantage of driving an EV has actually decreased compared to the advantage at the beginning of the project, which gave a fueling cost of one third compared to gasoline. This speaks to the volatility of gasoline prices – the cost of electricity has not changed significantly in the three years.

There are significant barriers to widespread EV use. Battery cost and limited drive range are major obstacles to mass adoption; significantly less expensive batteries with improved energy densities beyond that of Li-ion are required. This market has a major environmental effect, as the transportation sector represented 26% (27.1 quadrillion Btu) of total U.S. energy consumption in 2014, with light-duty vehicles (LDVs, almost entirely petroleum based) accounting for 55% of that [10]. Vehicle electrification offers the opportunity to significantly reduce U.S. energy consumption by shifting the personal transportation sector away from a sole reliance on petroleum to technologies that leverage our country's competitive advantage for innovation. At the project start, electric vehicle penetration was not expected to become significant until 2035. At project end, the outlook is more positive. In 2014, less than 0.5% of the 85 million cars sold in the world were electric; however, those sales account for half of the electric cars on the road today. The demand has grown so rapidly that the global market is expected to grow more than sevenfold by 2020. If government incentives for efficient vehicles increase, this may happen even more quickly [11].

As stated in the Introduction, assuming that the lower-cost, lighter weight Li-sulfur battery technologies enabled by the work accomplished in this Advanced Manufacturing Initiative program completely replace Li-ion batteries in EVs, and that EVs penetrate the LDV fleet by 2% and 5% in the years 2020 and 2030, the energy savings annually would be 100 trillion Btus (in 2020) and 250 trillion Btus (in 2030), based on improved well-to-wheel energy efficiency of PHEVs/BEVs relative to that of ICE vehicles [1,2]. Displacing ICE vehicles with EVs reduces petroleum usage, which could lead to a petroleum energy savings of more than 500 trillion Btus per year after the year 2030. This translates to on the order of 780,000,000 Mlb/year decrease in emissions of CO_2 per year. Implementing the Li-air and Li-sulfur batteries in grid energy storage applications could lead to further reductions in greenhouse gases. Of course, due to the lower TRL of our Li-S technology, the timeline for Li-S to penetrate the EV market may be in the 10-20 year range, so these benefits may be delayed to 2025 or 2035.

The overall economic impact ($/year) and market impact (% penetration) of PolyPlus' batteries by the year 2020 is likely to be small. Obtaining funds to scale up our manufacturing capacity and developing a customer base will take more than half of the five years between the project's completion in 2015 and the year 2020.

The global market for batteries is in the hundreds of billions of dollars per year, and the U.S. battery manufacturing industry makes up only a fraction of that at $12.5 billion. Less than ¼ of that is due to U.S. produced primary lithium batteries; this market is $3.1 billion/year [12]. The most likely first product to be manufactured by PolyPlus would be a primary Li/Seawater battery to be used by the Navy in passive sensing sonobuoys. The Navy currently uses other types of batteries for this purpose - PolyPlus' technology is lighter and longer-lasting - enabling the Navy to deploy the sonobuoys for longer periods of time. Government contracts for TRL advancement and prototyping will delay the full onset of production for a few years. Therefore, in the year 2020, PolyPlus is projected to produce Li-Seawater batteries for the Navy with yearly revenues of around $1-2 million. This translates to a primary battery market penetration of only 0.05%.

However if we project to the year 2025, optimistically assuming that all sonobuoys produced in the U.S. will use PolyPlus' Li/Seawater batteries, we can project a larger economic impact. We assume that the current budget for sonobuoys is on the order of $200 million at a unit price of $1400, and the battery pack is a fraction of that. If we assume that all the sonobuoys produced in the U.S. shift to the deep-drifting, long duration type that require Li-Seawater technology, the budget for sonobuoys would need to change dramatically, since the battery pack cost would increase. If PolyPlus were to supply enough battery packs for all sonobuoys in the U.S., the revenue would be upwards of $1 billion annually. In addition, demand for PolyPlus' Li-Air batteries can be estimated with the assumption that PolyPlus' Li-Air technology will replace a certain fraction of the batteries currently purchased for soldier power applications. Assuming just a 5% penetration of Li-Air cells into the soldier power market by 2025, revenues could be in the $300 million range annually. Finally, if the Li-S battery replaces Li-ion in its most common consumer applications, the economic impact would be in the hundreds of billions of dollars per year – however, the timeline for this market penetration would be even further off since the Li-S cell is at a lower TRL than the Li-Air and Li-Seawater.

6. Commercialization

6.1 Commercialization Status:

The commercialization plan for the PolyPlus batteries will be staged, due to the fact that there are three battery types at various levels of technology readiness and commercialization readiness. The Li-Seawater and Li-Air batteries are at a higher technology readiness level (TRL) than the Li-Sulfur batteries. For both the Li-Seawater and Li-Air technologies, PolyPlus has developed robust cell prototypes that have been tested in laboratory environments with good reproducibility. In contrast, as of September 2015, Li-Sulfur is still at the lab cell stage with potential prototype cells under development. Since considerable development work still needs to be done with the Li-S chemistry, this technology will not be commercialized for some years.

The commercialization of the Li-Water technology is closest at hand due to the fact that there is currently an application funded by a Future Naval Capabilities program with the Office of Naval Research (ONR) for which the volumetric and gravimetric energy density of PolyPlus' Type I Li-Seawater battery is essential. In parallel with the DOE-IMI program, PolyPlus obtained several small ONR Small Business Innovation Research (SBIR) contracts that advanced designs for Li-Water battery packs for use in passive sonobuoys. The Navy is expected to provide funding for building prototype battery packs based on these designs in the next few months (Fall 2015). Assuming successful demonstration of these packs at the end of the contract, the Navy intends to request funding from the Department of Defense Title III program to support manufacturing scale-up of PolyPlus' batteries over the next 5 years.

The commercialization of the Li-Air technology would occur through a similar mechanism, but through a different branch of Defense. The U.S. Army CERDEC has been a strong supporter of our Li-Air battery development. Working with the Army has been advantageous, because it has allowed PolyPlus to develop the Li-Air technology to the level that it could cover 90% of the man-portable power needs of warfighter for 72 hour missions. CERDEC not only defines the specifications to which the batteries need to perform, but it also serves as a third party tester to verify battery performance. CERDEC also serves as a portal to the various branches of the armed forces - their support should allow PolyPlus to identify the right first military customer for the cells. Upon successful completion of the current contract, PolyPlus will apply to CERDEC for a program that would fund the build of a battery pack for demonstration in a relevant environment. A military customer would need to confirm that this capability solves a problem for them, and would request funding from the Department of Defense's Title III program to support manufacturing scale-up of the technology.

As stated above, the Li-Sulfur technology is further from commercialization than the other two technologies. CERDEC has expressed interest in funding further development of our Li-S batteries. A few development contracts with this institution would advance the TRL and CRL of the Li-S technology to the point at which it could be commercialized. In addition to these activities, PolyPlus is exploring additional funding opportunities for the development of the Li-Sulfur battery with ARPA-E, USABC, the Vehicle Technologies Office, and will continue to discuss partnership options with battery and automotive companies.

6.2 Title III Program:

Funding for manufacturing scale-up could potentially come from the Title III program of the Defense department. The mission of Title III is to fund production capabilities and capacities for items essential for national defense, but that also have applications in commercial markets. PolyPlus has met with the Department of Defense Title III office, and submitted to the 2015 Title III RFI regarding our Li-Seawater and Li-Air products, which already have potential military and commercial customers. If a program office in the Army or Navy determines that one of PolyPlus' battery products is essential to one of their missions, they can advocate for PolyPlus to receive funding from the Title III program for manufacturing scale-up. At that time, PolyPlus would need to prove that the technology is also of interest to commercial markets.

The high performance and reproducibility of the PLEs produced by the PolyPlus pilot line aids our efforts to court strategic partners and investors for prototype development, engineering support and scale up. PolyPlus is actively engaged in talks with large automotive companies, offshore oil & gas exploration companies, the US Navy, and intelligence agencies regarding its ultra-high energy density lithium-seawater battery technology, and the US Army for its ultra-light Li-Air battery technology. We are also seeing high levels of interest from a number of automotive and consumer electronics firms interested in our rechargeable Li-S battery technology.

7. Accomplishments

During Q2 of the project, one of the most significant accomplishments was completed: the design, shipment, and installation of the pilot production line for the first-of-its-kind semi-automated manufacturing of PolyPlus' proprietary Protected Lithium Electrode (PLE). This line is currently in operation at PolyPlus' Berkeley, CA, facility after being delivered in February 2013. The final equipment design resulted from a coordinated effort between the large Japanese equipment manufacturer and PolyPlus, with constant examination of parts produced on the line during development and critical feedback provided by PolyPlus. In fact, one important piece of equipment had to be redesigned after PolyPlus engineers discovered a design flaw (and the fix was promptly executed). After installation and staff training, PolyPlus subsequently performed troubleshooting and shakedown of the new manufacturing equipment by producing PLEs in limited batches. A minor design flaw was discovered during this time that resulted in excess material waste in a single step when operating the equipment at an output rate below the rated throughput. A custom engineering solution to mitigate this issue when running small, lab-sample batches, was developed and implemented. Further necessary modifications, improvements, and redesigns were identified and executed as the manufacturing technology improved. Significantly, PolyPlus demonstrated during the third quarter (Q3) that the PLE's produced on the pilot line matched the performance of PLE's assembled manually, an important milestone in this program, achieved less than 5 months after initial installation of the first-of-its-kind pilot production line.

During Q2 and Q3, Corning replicated the PolyPlus PLE-testing set-up, based on exceptionally detailed engineering drawings, electrochemical test rigs, and other descriptions provided by PolyPlus, and instituted methods to begin characterizing solid electrolyte membranes in a consistent manner with the techniques and practices used at PolyPlus. Bringing this full testing capability in-house has helped to accelerate Corning's evaluation of solid electrolyte production progress. Corning also commissioned a larger and higher volume lab-scale tape-caster to investigate scale up and enable larger volume sampling of solid electrolyte membranes for evaluation in PolyPlus labs. Organizational changes were also made on the Corning project team, focused on bringing in personnel with seasoned manufacturing experience to work through small-volume scale-up issues that impact solid electrolyte quality. Process controls and more rigorous change tracking were introduced in Corning research labs to accelerate development turns and minimize solid electrolyte sample variability away from PolyPlus specifications.

At the end of Budget Period 1 (Q4), PolyPlus and Corning successfully met all the program Go/No-Go criteria, and the continuation application was approved for the team to move into Budget Period 2. The Go/No-Go milestones focused mainly on the performance and stability characteristics of solid ceramic electrolyte membranes and their use in PolyPlus PLE's. A large focus was on improving materials properties of the Corning-produced Li^+ ion conductive solid electrolyte plates. Membranes with room-temperature ionic conductivity $>1x10^{-4}$ S/cm were demonstrated and shown to be pinhole free and chemically stable in the Li-seawater and Li-air battery operation environments (seawater and PolyPlus' aqueous electrolyte, respectively). Further, lab-scale batch-produced Corning membranes were shown to have sufficient mechanical strength and flatness to survive the PolyPlus PLE assembly process.

During Q5, Corning solid electrolyte membrane samples were provided in larger volumes to PolyPlus, but persistent failures were seen when fabricated into PolyPlus PLEs. This process scale up identified multiple issues with the solid electrolyte samples, particularly part flatness and surface defects that impacted mechanical quality. Due to the brittle nature of the solid ceramic electrolyte materials explored, any significant out-of-plane form deviation cannot be tolerated in the PolyPlus PLE fabrication process, as significant mechanical stress is otherwise introduced when parts are subjected to pressure during the PLE assembly process. Corning continued to improve both long- and short-period surface form to achieve parts that could survive the PolyPlus PLE assembly operation, optimize precursor contaminant control as well as casting and firing process uniformity and reproducibility, and worked towards providing PolyPlus with monthly regular volumes of larger size solid electrolyte samples.

During Q6, Corning progressively improved the solid electrolyte plate mechanical strength. The strength improvements have resulted from further optimizing the conditions, including firing schedule, in the production process. PolyPlus, meanwhile, designed and instituted a new testing procedure to help identify the failure mechanism(s) of the solid electrolyte plates during PLE assembly and ensure quality control. PolyPlus assembled single-sided samples consisting of a Corning solid electrolyte plate and the hermetic compliant seal structure. Rather than a lithium electrode, the sample structure was filled with a methylene blue solution used to illustrate cracks or defects in the membrane, seal, or interfaces. This assembly subjected the solid electrolyte plates to the mechanical stresses and heat-sealing process used in PLE manufacturing. PolyPlus also continued to improve the pilot manufacturing line, having replaced plastic lines with stainless steel, and trouble shooting software glitches.

During Q7, the PolyPlus team spent a significant fraction of its time improving the pilot line, including retrofitting the line for intermittent operation, modification of semi-automated PLE assembly procedures and working with the vendor to improve software control/monitoring of the line. The pilot line now functions as expected and allows PolyPlus to fabricate PLEs in a reproducible fashion and at high yield (> 90%). PolyPlus has also done extensive testing of solid electrolyte membranes supplied by Corning (U.S.) and Ohara (Japan) with regards to stability against aqueous polysulfides. Since the market for lightweight rechargeable lithium-sulfur batteries may be very large, Corning has narrowed its focus on optimization of solid electrolytes for Li-S batteries. PolyPlus has initiated preliminary studies to determine the chemical stability of Corning membranes in contact with aqueous polysulfides; early results indicate that Corning membranes do not show the characteristic signs of chemical reduction on exposure to polysulfides ($Ti^{4+} \rightarrow Ti^{3+}$) which we typically see when solid electrolytes supplied from Japan are exposed to the same solutions.

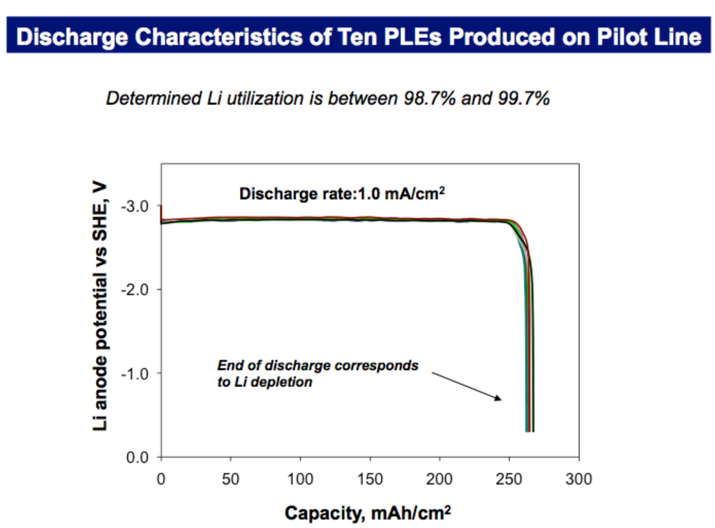
During Q8, PolyPlus and Corning successfully met or exceeded all of the Go/No-Go criteria required for completion of Budget Period 2 of this Advanced Manufacturing program. The Go/No-Go criteria focused mainly on the process development for LATP membranes, including mechanical testing and performance and stability optimization of the membranes, pilot line production of Li-Water, Li-Air, and Li-S PLEs, and electrochemical evaluation of PLEs in batteries. The program was successful and on-schedule to date; at the time of the continuation application submission, the pilot-produced PLEs had been tested in battery configuration, and the reproducibility and quality of the results of electrochemical testing were very high.

During Q9, PolyPlus and Corning successfully completed the required milestones. PolyPlus' task was for the Li-water cells to hit the commercial targets. Cells were evaluated against the target performances by measuring mass, volume, electrochemical discharge capacity, cell potential, discharge rate, and chemical stability. Corning's task was to deliver 6 garnet membranes with conductivity >10^{-4} S/cm for lithium contact testing. These samples were delivered to PolyPlus, where initial Li stability and cycling tests were initiated. The membranes' DC conductivity was measured by PolyPlus to be 1.4×10^{-4} S/cm. The cycling results for Li/liquid electrolyte/garnet/liquid electrolyte/Li were encouraging for early testing: they showed that the garnet cycles smoothly and that there is a decrease in polarization on cycling. Testing of Corning LATP membranes in Li-S cells has been ongoing for the past few quarters. The membranes are stable to the sulfur catholyte, and have successfully cycled almost 100 times. In addition, during Q9 PolyPlus and Corning submitted to the DOE a modified Project Management Plan including a Statement of Work that reflected Corning's change of scope for Budget Period 3.

During Q10, PolyPlus completed its milestone for the Li-air cells to hit the commercial targets. PolyPlus' military partner in the development of Li-Air cells visited our labs to view the pilot line and talk about the requirements that must be met before the Li-Air cells can be acquired and used by military customers. There were no milestones for Corning during this reporting period; however, Corning representatives visited PolyPlus to report on their progress toward fabricating the next set of garnet pellets, and tape cast samples. PolyPlus continued electrochemical testing of the garnet and LATP samples from Corning, and the results are reported below.

During Q11, PolyPlus completed its milestone for the Li-S cells to hit the commercial targets. Corning completed its feasibility study for membrane production, and also shipped 6 garnet membranes with <15 micron grain size and 3×10^{-4} S/cm conductivity to PolyPlus for electrochemical testing. PolyPlus continued electrochemical testing of the garnet and LATP samples from Corning.

During the final reporting period, PolyPlus and Corning both completed the required milestones. Corning delivered 11 tape-cast garnet membranes to PolyPlus on 9/15/15, and PolyPlus is in the process of preparing them for electrochemical testing. PolyPlus demonstrated that PLEs could be produced on the pilot line at the required rate and yield, and measured their electrochemical performance in various battery cells, with >90% lithium utilization, as shown in the figure below. The PLEs produced on the pilot line have such consistent discharge performance that the data is overlapping.



Further accomplishments: The updated website for PolyPlus Battery Company www.polyplus.com includes images of PLEs, Li-Water, Li-Air, and Li-S cells built on the pilot line, as well as images of the pilot line itself.

8. Conclusions

This PolyPlus-Corning IMI project resulted in the successful installation and demonstration of a novel, semi-automated pilot line for the manufacture of PolyPlus' patented Protected Lithium Electrode (PLE): a central battery component for the next generation of lightweight energy storage technologies including Li-Air, Li-Water, and Li-Sulfur batteries. In addition, PolyPlus and Corning worked together to develop a scalable production process, as well as a new formulation for the ceramic membrane component of the PLE. This pilot line is the first step along the pathway to full scale manufacturing of a technology that represents a step-change, rather than an incremental development, in high performance, cost-effective batteries. This new class of batteries has the potential to overcome the limitations of the ubiquitous Li-ion batteries used today, and with scale-up and commercialization will have a significant impact on the portable electronics industry, as well as the electric vehicle industry, leading to reductions in greenhouse gas emissions.

Developing our first customers is the next great challenge. The excellent performance and reproducibility of the PLEs produced by the PolyPlus pilot line will strongly support our commercialization efforts. As described above, PolyPlus is already under contract with two different military customers to further develop and demonstrate the performance of our Li-Air and Li-Water cells. In addition, PolyPlus is in discussion with several large commercial battery firms regarding licensing and/or partnering to scale the rechargeable lithium technology.

9. Recommendations

Recommendations for future work include the following:

To upgrade the pilot line, PolyPlus Battery Company in tandem with the battery manufacturing engineering firm will need to work on designing methods for manufacturing PLEs and battery prototypes with alternative seal designs. In addition, the two companies should discuss the design and costs of full automation of the line for high volume production. This would include the integration of quality assurance and quality control testing into the production line.

Cost modeling of the Li-conductive ceramic membrane at Corning shows meeting the membrane cost targets for electric vehicle application will be challenging due to relatively high processing costs of tape cast ceramic membranes compared to conventional polymer separator and liquid electrolyte. To achieve membrane cost well below $\$100/m^2$, as needed to achieve aggressive electric vehicle cell cost targets, new approaches to electrolyte manufacturing will likely be required.

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