Methanol Fuel Cell Enabled Hybrid Power System

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Technical Category and Subcategory: 7.L Technologies for portable power applications & 3.D Technologies for improved fuel cells specifically for transportation applications

Estimated Total Project Cost: $3.6M

Project Duration: 3 years

**Summary**

Next generation portable electronics, remote monitoring and communications systems will increasingly require always-on technologies – such as powered sensors, continuous data acquisition, on-chip data analytics and communication– to improve functionality and extend into applications currently prohibited by relatively high energy demands.

Lithium ion batteries are sufficient to power existing portable systems, and operate at or near 100% Coulombic efficiency over both a wide state of charge and a wide range of currents. But low energy densities, below 150 Wh/kg (100 Wh/L), place prohibitive limits on the always-on state required for next generation functionality in portable devices, such as cellular phones and tablets.

Direct methanol fuel cells have theoretical energy densities in excess of 5000 Wh/kg (3000 Wh/L), but suffer from intrinsic electrochemical limitations to their use as stand-alone power supplies. Sluggish kinetics, and chemical-, mass transport-, and ohmic-polarization losses impede their ability to promptly respond to changes in power demand and result in a narrow optimal operating range, respectively.

A hybrid battery-fuel cell power system couples the energy density of a direct methanol fuel cell (DMFC) with the power response and wide operational efficiency of lithium ion batteries (Li-ion).

This project will, over three years, address the three challenges facing direct methanol fuel cells that impede their commercialization: high methanol crossover, high activation polarization, and poor anode catalyst longevity due to Ru dissolution. In order to reduce battery complexity, and improve the volumetric energy density, this project will improve battery technology through the development of a solid-state lithium ion battery.

**Innovation and Impact**

A hybrid DMFC/solid-state lithium ion battery system will have a positive impact across several mission areas of ARPA-E. Methanol is currently produced at commercially viable levels by steam reforming natural gas, which the United States has in abundance, which would significantly reduce our dependence on foreign sources of liquid fuels. Furthermore, methanol may be produced from biomass through a syngas intermediate, reducing the production of greenhouse gases.

This technology could significantly improve the efficient use of energy in the United States. Domestically, portable electronics (laptops, tablets, and cellular phones) operate on an estimated 87.5 gigawatt-hours per day.

Limited by Carnot efficiency, power generation from fossil fuel-fed heat engines range in efficiency from 25% (petroleum-fed gas turbine) to 45% (natural gas-fed combined cycle), averaging 33%, excluding transmission losses. Therefore, powering portable electronics require an effective energy of 262.5 GWh per day.

The use of methanol reduces electrical losses, increasing energy efficiency, by enabling distributed power generation. Steam reforming methane to syngas ranges in efficiency from 80-90%, from syngas to methanol, > 99%; and electrooxidation of methanol, thermodynamically limited to 97%. The sets an upper limit on the fuel-to-use efficiency between 77% and 87% and lowers the effective, daily energy requirement of portable electronics from 262.5 GWh to 113.6 GWh.

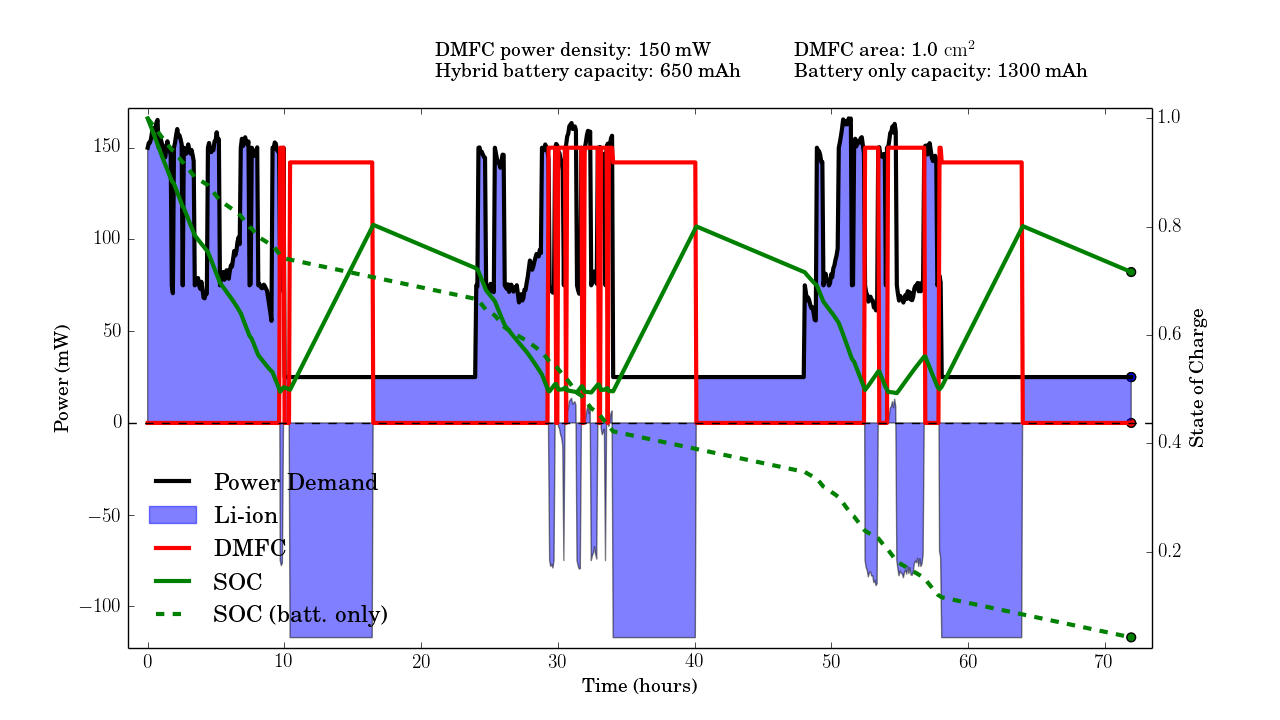


Figure Simulated power usage for a cellular phone operating over 72 hours. The hybrid power system maintains its battery in an optimal state of charge, between 50% and 80% while simultaneously limiting high frequency variations in the power demand for the DMFC. Negative values in power indicate a battery charging cycle.

Charge cycling for laptops and cellular phones is typically characterized by some level of discharge, occasionally deep, followed by a charge-and-hold at capacity, e.g. while at a desk or while charging overnight. Such cycling deleteriously impacts the performance of lithium ion batteries by activating redox reactions at the anode and cathode. By maintaining the hybrid power system’s component battery between 50% and 80% minimizes, or even eliminates these reactions.

Several technical challenges must be overcome that will improve the performance of a hybrid direct methanol/solid-state battery hybrid power system, these include challenges to the GO membrane, the catalyst layers, and to the lithium ion battery.

The theoretical energy density of DMFCs is reduced significantly by methanol crossover. Crossover current is made up of contributions from convective, diffusive, and electroosmotic drag. The latter dominates the crossover current densities in excess of 200 mA/cm^2. (Bahrami2013) As electroosmotic drag is directly proportional to the methanol concentration at the interface, the fuel concentration is lowered from concentrated methanol (~24.7 mol/L) to < 2 M. While this does improve performance by reducing crossover, it also significantly lowers the energy density of the fuel. The proposed effort will use GO as a DMFC membrane to reduce methanol crossover, and will increase proton conductivity through the degree of oxidation and the chemical modification of the GO membrane. The density of GO surface defects impacts the proton conductivity, but neither the magnitude of this effect nor the effect on methanol crossover have been characterized. Similarly, through-platelet conduction is thought to occur through a proton transport mechanism that involves proton acceptor sites on opposing faces of a GO sheet. Chemical modification of these sites is thought to improve this mechanism. This work will use dry chemical methods and ALD to chemically modify the GO surface without introducing additional structural damage to the GO sheet.

Complete electrooxidation of methanol involves the formation of carbon monoxide, which poisons the platinum catalyst. Extensive study has revealed that a Pt-Ru alloy is stable against CO poisoning, but dissolution of Ru in the acidic environment of the DMFC anode limits anode catalyst longevity. The proposed effort will increase catalytic activity by optimization of the catalyst synthesis to produce nanoparticles of prescribed morphologies, shapes and sizes. We will pursue the catalyst optimization by developing research synergies that combine computational tools (search algorithms, synthesis models, simulations of process or properties, etc.) with experimental methods/techniques of synthesis and characterization in order to predict desired materials and to achieve a fundamental understanding of their synthesis and/or control over the final product and its catalytic properties. The catalytic materials systems to be addressed in the proposal are metal nanoparticles (NPs), with or without core-shell morphologies. These well-defined catalytic systems are ideal for linking experiments and modeling, providing controlled systems for building selective and complex functionalities. The proposed effort will increase catalyst stability by lowering the solubility of Ru in acidic media. This will be done by… (Steve)

Solid-state electrolytes appreciably reduce the complexity of each lithium ion cell, reducing both weight and volume. Able to sustain a prescribed power- and short-term energy-requirement with a smaller cell, this volume and weight can be recaptured into increased fuel storage, multiplying the impact of any improvement in battery performance. An all solid-state battery using solid electrolytes instead of organic liquid electrolytes is expected to have higher energy density than a lithium ion battery using organic liquid electrolytes and having a bipolar stack structure. Furthermore, use of solid-state electrolytes will improve the safety and reliability of lithium secondary batteries. All-solid-state batteries can be divided into two types, thin-film-type and bulk-type. For large-scale applications, bulk-type lithium-ion batteries (ASSLBs) with high loadings of active material and solid electrolyte powders, are well suited because of their high energy density. However, ASSLBs have crucial challenges for the practical applications, such as poor rate performance and poor contact between the active material and the electrolyte. In order to overcome the problem of low ionic conductivity in solid electrolytes such as LiPON, sulfide type electrolytes were developed. Sulfide-based solid electrolytes Li2S–P2S5 and Li2S–P2S5–GeS2 systems offer ion conductivity from 10-3 to 10-2 S cm-1 at room temperature, similar to liquid electrolytes; and they have a high decomposition potential of 5 V. With these electrolytes, the maximum resistance is observed at the cathode/sulfide electrolyte interfaces. Thus, understanding the cathode/electrolyte interface has become an issue of the greatest importance for the improvement in ASSLBs.

This result will be transformational because operating at a higher methanol concentration has the potential to introduce a 12 to 40 fold increase the energy density of existing direct methanol fuel cells. Current DMFCs using Nafion® polymer membranes operate at a methanol concentration between 0.5 and 2 M. This lowers methanol crossover, improving the operating voltage and power density of the cell, but at the expense of a fuel with significantly lower energy density. At these methanol concentrations, the energy density of DMFCs are in line with, or slightly below, Li-ion batteries. Any significant improvement in the energy density of the DMFC, two-fold or greater, would result in a technology…

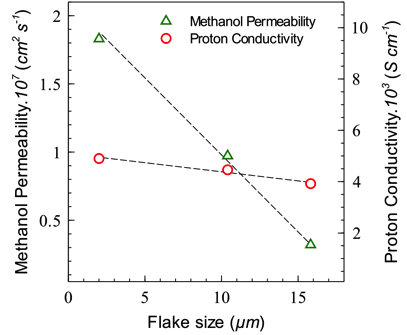


Figure Methanol permeability (diffusivity) and proton conductivity through graphene oxide (GO) as a function of the mean nanoplatelet size. From Paneri2014.

Graphene oxide (GO) has recently been shown to be an incredibly selective, semipermeable membrane, with water permeability greater than four orders-of-magnitude (OOM) higher than that of helium gas, ethanol, and acetone. Initial investigation into graphene oxide as a high-methanol concentration DMFC membrane has proven to be very promising, with proton conductivity 4 OOM lower than Nafion®. This has enabled methanol concentrations 2.5-5 times larger than are typical for Nafion®-only membranes.

The naissance of this membrane leaves many questions open. Among them is the effect of chemical modification on the transport properties of GO. Wet chemical methods have been used to sulfonate GO, which improved proton conductivity, but negatively impacted methanol impermeability. To improve the proton conductivity, we will use atomic layer deposition (ALD) and dry chemical methods to modify GO in the following ways…

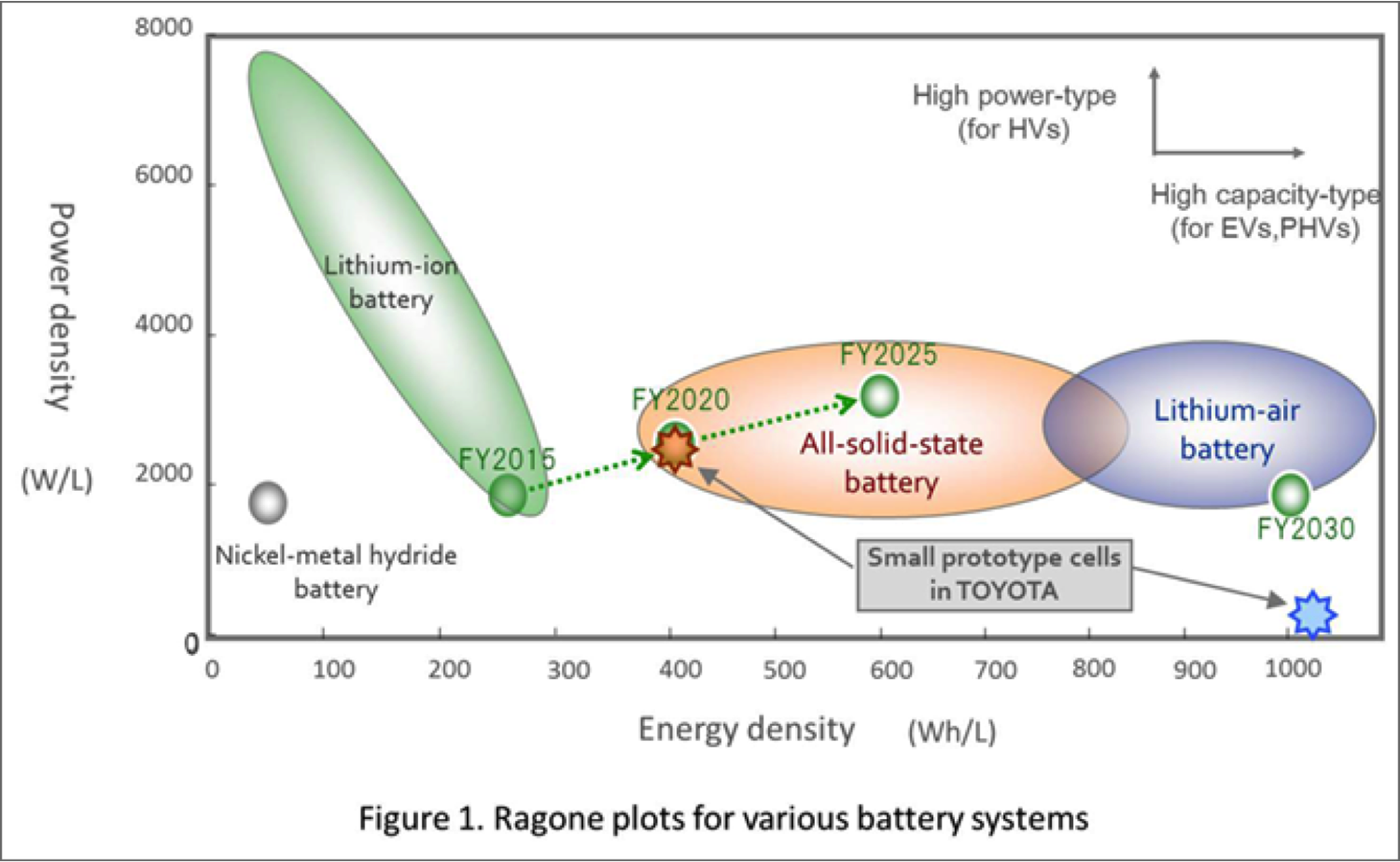


Figure Ragone plot showing the timeline for the expected improvement in proton exchange membrane fuel cells over the next decade. With a higher volumetric energy density, methanol is expected to display higher power and energy densities.

Ohmic losses result from a proton conductivity in GO that is one-tenth that of Nafion 117. In addition to chemical modification of GO, the physical characteristics of GO also play a role in methanol permeability and proton conductivity: platelet size, film thickness, and relative humidity.

Compared to existing and emerging technologies, a hybrid solid-state battery/fuel cell power system will be disruptive. Currently, DOE targets 300 Wh/kg for lithium ion batteries, which will require significant improvements across all aspects of the lithium ion battery. Balance of plant structures in current and emerging Li-ion battery technologies set an upper bound of 195.74 Ah/kg. A 36% increase in *both* anode and cathode capacities, operating at 3.6 V, is required to meet five year energy targets of 300 Wh/kg. Although 4.8 V, high voltage spinels can theoretically achieve the 300 Wh/kg target, at these voltages electrolyte decomposition raises serious safety concerns. But even with these targets, still several years out, are achievable by an 18 M direct methanol fuel cell operating at 0.4 V.

Solid state batteries hold the promise to lower the parasitic losses that result from the balance-of-plant structures in existing Li-ion chemistries by reducing each cell from current collectors, separators, lithium salt, electrolyte, anode, and cathode to current collectors, anode, cathode, and electrolyte. Reducing the mass of balance-of-plant structures by 50% would increase the capacity of existing graphite/LiCoO2 batteries by 15%. Absent electrolyte breakdown concerns, high voltage spinels would lead to a 20% increase, without requiring discovery of new electrode compounds.

Direct methanol fuel cells combine the use of high energy density fuels typical of high temperature solid oxide and phosphoric acid fuel cells with the low operating temperature of hydrogen fuel cells. A commercial attempt at solid oxide fuel cells for portable applications was able, through extensive developments in most aspects of cell design, to lower radiative losses by nearly two orders of magnitude. Absent cogeneration however, and despite these advancements, radiant losses accounted for ~50% of the energy generated by this system, ultimately rendering this system unviable. Furthermore, thermal cycling of these high temperature fuel cells and the highly corrosive electrolyte of phosphoric acid fuel cells severely limit longevity in the highly cyclical nature of portable energy generation.

Commercialization of hydrogen fuel cell-battery hybrid systems raises questions about the disruptive and transformative potential of a DMFC-battery hybrid. However, while liquid hydrogen has a significantly higher energy density by mass, cryogenic hydrogen is impractical for portable applications. Methanol has ten times (two times) the gravimetric (volumetric) energy density of hydrogen stored as a metal hydride, and, because it is liquid at room temperature, greatly simplifies both handling and distribution.

Several technical performance targets are necessary to realize a disruptive technology.

DMFC

present methanol concentration: 2 M

target methanol concentration: > 10 M

present methanol permeability: 50 mA/cm^2 (Zhao2009) – 200 mA/cm^2 (Corti2014; Gottesfeld S, Minas C (2008) Optimization of direct methanol fuel cell systems and their mode of operation. In: Kakac ¸ S, Pramuanjaroenkij A, Vasiliev L (eds) Mini-micro fuel cells. Springer, Dordrecht, pp 257–268)

target methanol permeability: 0.25 mA/cm^2

present proton conductivity: 4-5 x 10^-3 S/cm (Paneri2014)

target proton conductivity: in line with Nafion, 0.001 - 0.08 S-cm^-2 (20% - 100% RH, respectively. Sone1996)

present cost: $55/100Wh = $550/kWh (Han J, Liu H. Real time measurements of methanol crossover in a DMFC. J Power Sources 2007;164:166–73; Kamarudin2009)

target cost: $50/200 Wh = $250/kWh

Solid state battery

lithium conductivity:

operating temperature:

energy density:

present cost: $145/100 kWh = $1450/kWh (Han J, Liu H. Real time measurements of methanol crossover in a DMFC. J Power Sources 2007;164:166–73.; Kararudin2009)

target cost: $100/100 kWh = $1000/kWh

**Proposed Work**

Year 1 will focus on the development of individual components with significant improvements toward the target performance metrics. This will include:

* Synthesis and characterization of candidate graphene oxide and chemically modified GO membranes: proton conductivity, methanol permeability, and temperature sensitivity. Modifications to GO will include… Molecular dynamics simulations of defects on the graphene oxide surface, and their proton transport mechanisms will be used to evaluate the efficacy of chemically modified GO membranes.
* Synthesis and analysis of the stability, activity, and performance of the anode catalyst layer under conditions near and around those expected during fuel cell operation. Improvements to the catalyst will involve modeling (Cristian) and growth/deposition of Pt-Ru alloy nanoparticles (Steve).
* Synthesis and characterization of a solid state battery electrolyte: lithium conductivity, cycle stability, …

In addition, system level modeling efforts will be put in place to pre-optimize operating conditions based on the properties of gas diffusion layer, catalyst layer, and membrane.

Year 2 will focus on the achieving the target performance metrics for all individual components. Fuel cell components will be integrated into a test cell for controlled performance testing at the Energy Systems Integration Facility at NREL. Solid-state battery components will be integrated into a coin cell configuration for electrochemical testing.

Year 3 will optimize the performance of the integrated fuel cell and battery systems under simulated real-world operational variations. Merging the fuel cell and solid-state battery into a hybrid power system will be done at PGI.

These goals are realistic based on the following background, simulation, modeling, and experimental data.

Following discovery of its remarkable selectivity, GO was rapidly identified as a candidate membrane for DMFCs. However, intrinsic properties – such as low proton conductivity and high thermal sensitivity – have limited its use up until now as a membrane in DMFC.

Chemical modification of GO has been seen to improve the proton conductivity to values within the range of Nafion® (Sott2012a), but other reports indicate a corresponding increase in methanol permeability (Jiang2014). Sulfonation has been shown to significantly increase proton conductivity at low methanol concentrations (Jiang2012), but at higher concentrations, the sulfonic acid groups on the GO surface induce a methanol/water phase separation that reduces proton conductivity (Paneri2014). The precise nature of proton transport through GO is not known, but the insensitivity of proton transport to flake size (Fig. X) suggests through-platelet transport plays a dominant role; contrarily, the large drop in methanol permeability over that same range indicates methanol permeation occurs predominantly at platelet edges. It is thought that this phase separation phenomenon does not occur with the non-sulfonated GO surface defects because of their lower acidity. What methods and modifications have we at our disposal; ALD: Al, S, TM; dry chemical methods: ??

PGM activity has been seen to increase on novel substrates, such as CNT and ceria (Feng2013a), and is known to have a significant NP shape dependence. What work has been done in addressing catalytic activity?

What work has been done in ASSLB?

By combining battery technology with direct methanol fuel cells, advancement in this hybrid system does not hinge on improvement in any single technology, but rather benefits from every individual improvement: in battery capacity, catalyst activity, or membrane performance.

Key technical risks include…

Technical risks will be mitigated by…

Several techno-economic challenges exist that stand in the way of commercialization. Both anode and cathode require platinum and platinum-group metal catalysts. Typical loading levels, 2.5 mg/cm^2 on each catalyst layer, account for a price of $1366/kW, based on platinum at $1162/oz. At this cost, the price per kilowatt is prohibitive.

**Team Organization and Capabilities**

􏰀  Indicate the roles and responsibilities of the organizations and key personnel that comprise the Project Team.

􏰀  Provide the name, position, and institution of each key team member and describe in 1‐ 2 sentences the skills and experience that he/she brings to the team.

􏰀  Identify key capabilities provided by the organizations comprising the Project Team and how those key capabilities will be used in the proposed effort.

􏰀  Identify (if applicable) previous collaborative efforts among team members relevant to the proposed effort.