Integration and Optimization of Novel Ion Conducting Solids (IONICS) Program Overview

B. PROGRAM OVERVIEW

1. SUMMARY

The Integration and Optimization of Novel Ion Conducting Solids (**IONICS)** program seeks to enable transformational electrochemical cells by creating *components* built with solid ion conductors that have a wide range of desirable properties including low ionic area-specific resistance (ASR), high chemical and electrochemical stability, high selectivity, good mechanical properties, *etc.* through innovative approaches to overcome tradeoffs among coupled properties. It also seeks to develop and apply methods for processing of solid ion conductors and their integration into electrochemical devices. Components built with solid ion conductors, especially separators, have the potential to serve as enabling platforms, as demonstrated by the wide application of Yttria-Stabilized Zirconia (YSZ) ceramics and perfluorosulfonic acid (PFSA) polymers (*e.g.*, Nafion®). The IONICS Program Categories focus on specific electrochemical cells with high impact for the energy sector whose commercial potential will be significantly enhanced with improved components built from solid ion conductors. The Program Categories include:

1. Lithium (Li) ion conductors that enable the cycling of Li metal without shorting
2. Selective and low-cost separators for batteries with liquid reactants (*e.g.*, flow batteries)
3. Alkaline conductors with high chemical stability and conductivity
4. Other approaches that could achieve the IONICS Program Objectives.

A key requirement of the IONICS program is the creation of manufacturable components with dimensions comparable to that used in a practical device, in order to ensure that technical challenges associated with large-area processing are addressed. The required area depends on the application, but is in the range of tens to one hundred square centimeters. A second key requirement is that the cost of materials and processing is sufficiently low to allow for the broad adoption necessary for significant energy impacts. Creating low-cost components built with solid ion conductors will require pushing the boundaries of processing methods, especially for inorganic materials. ARPA-E encourages the formation of teams that include the competence to address large-area fabrication and low-cost processing.

ARPA-E expects that common technical themes will be present across the Program Categories. These themes may include, but are not limited to, polymer/inorganic composites, chemistries that realize high stability, processing methods for large-area and thin inorganic solid ion conductors, polymer and polymer composite morphology engineering, self-forming mechanisms, and others. ARPA-E expects that the realization of the aggressive targets of the IONICS program will require input from communities such as solid state ionics, polymers, ceramics, material mechanics (especially at interfaces), functional glasses, organic and inorganic chemistry, computational approaches across a range of length scales, and process engineering and scale up.

2. PROGRAM CONTEXT AND BACKGROUND

The electrochemical cell couples chemical reactions with electron flow external to the cell. It therefore provides a direct path to convert the chemical energy stored in materials such as natural gas, hydrogen, battery active materials, *etc.* into electricity. It also provides a direct path to store carbon-free intermittent renewable energy in chemical bonds, including as embodied energy in industrial products (e.g., Al) and in battery active materials that allow a return to electricity at a later time. These foundational capabilities of electrochemical cells are accompanied by two additional benefits: (1) high round-trip energy efficiency that in many cases has been realized practically (e.g., Li-ion cells can provide 90% round-trip DC-DC efficiency at relevant rates) and (2) scalability across a wide range of power levels (*i.e.*, <1 kW to >1 MW), making them suitable for both small, distributed and large, centralized installations.

Electrochemical devices have received research and development funding for many classes of batteries, transportation and stationary fuel cells, water electrolyzers, industrial electrochemical reactions, and other devices and processes. Several previous ARPA-E programs have pursued advances in electrochemical devices and processes, including Batteries for Electrical Energy Storage in Transportation (BEEST), Grid-Scale Rampable Intermittent Dispatchable Storage (GRIDS),

Robust Affordable Next Generation Energy Storage Systems (RANGE), Modern Electro/Thermochemical Advances in Light-metal Systems (METALS), Reliable Electricity Based on Electrochemical Systems (REBELS), and many projects within the OPEN portfolios.[1] The aforementioned ARPA-E programs have principally focused on advances at the *device* or *process* level. ARPA-E funded work complements significant research and development efforts on electrochemical devices within other parts of the Department of Energy, including Basic Energy Sciences, Energy Efficiency and Renewable Energy, and the Office of Fossil Energy. Based on the observation of key challenges encountered in previous ARPA-E programs and in other research and development efforts, ARPA-E believes tremendous opportunities exist in developing a new generation of enabling components built with solid ion conductors.

There are many classes of ion conductors, including aqueous and nonaqueous salt solutions, solid ceramics, polymers and polymer gels, molten salts, and others. Electrochemical cells that operate near ambient temperatures typically use either a liquid electrolyte (*e.g.*, aqueous H_2SO_4 in the case of lead-acid batteries, or $LiPF_6$ in organocarbonates in the case of Li-ion batteries) or a polymer containing small molecules (*e.g.*, hydrated PFSA in the case of fuel cells and electrolyzers). ***While liquid electrolytes have benefits including high conductivity and excellent wetting of electrode surfaces, this program is specifically focused on electrolyte attributes unattainable with liquids, including resistance to deformation (i.e., a "solid" form), wide thermal stability, high selectivity for desired ions and neutral molecules, and other attributes detailed through this FOA.***

To provide context and background for the challenges the IONICS program will address, the remainder of this section will describe some of the tradeoffs and challenges facing solid ion conductors using specific examples for inorganic and polymeric materials. A simple way to visualize the properties required of a component built with a solid ion conductor is a radar plot with property values along the axes. Figure 1 shows such a radar plot for three exemplary Li^+-conducting inorganic materials, with the following axis labels:

- The ionic area-specific resistance (ASR) helps determine the power capability of an electrochemical device; it includes the ionic conductivity (an intrinsic property) and the thickness (an extrinsic property).
- Selectivity is the ability of a material to transport ions and neutral molecules at different rates, with a goal of high selectivity for a desired species, typically a single ion.
- (Electro)chemical stability refers to both electrochemical stability and chemical stability, the former generally referring to stability as a function of an applied potential. In the ideal case all adjacent phases in a device are thermodynamically stable against reaction; in practice, stability is frequently realized with the help of slow kinetics and the formation of passivating layers.
- The electronic ASR reflects resistance to electronic current, and includes the electronic conductivity and thickness. For a separator, the electronic ASR is ideally infinite, while for mixed conductors within electrodes a low ionic and electronic ASR is desirable.
- Thermal properties refers to the dependence of key properties like ionic and electronic ASR, (electro)chemical stability, mechanical properties, *etc.* on temperature. Ideally, a component is able to conduct current, resist degradation, and remain strong and tough across a wide range of temperatures.
- Mechanical properties are critical both during both fabrication (*e.g.*, for roll-to-roll processing the tensile strength and ability to wind around a mandrel are relevant) and during operation (*e.g.*, a high shear modulus is theorized to prevent shorting during cycling of Li metal).
- Processing refers to the method used to create components built with solid ion conductors, and cost includes both the processing cost and the bill of materials.
- Device integration refers to the ability to integrate components built with solid ion conductors with other device components, as well as the implication of the components built with solid ion conductors on other device components (*e.g.*, existing PFSA membranes require the use of costly Pt for the oxygen electrode catalyst).
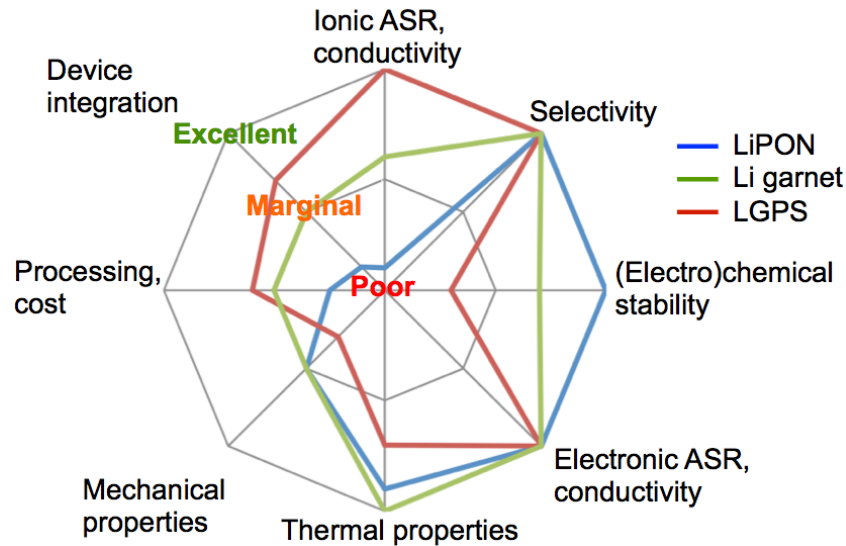
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[1] http://arpa-e.energy.gov/?q=arpa-e-site-page/view-programs

Figure 1. Radar diagram showing the qualitative attributes of three inorganic Li-conducting materials. LiPON = $Li_xPO_yN_z$, Li garnet refers to a crystal structure family (example composition: $Li_7La_3Zr_2O_{12}$), LGPS = $Li_{10}GeP_2S_{12}$.

One of the materials in Figure 1, LiPON ($Li_xPO_yN_z$ where x = 2y+3z−5) is an amorphous material that has a low conductivity for Li^+ (~1E-6 S/cm at 25°C, which for a typical thickness of 1 μm results in an ionic ASR of 100 Ohm-cm^2) but excellent electrochemical and (electro)chemical stability. It is deployed commercially in thin-film batteries composed of Li metal as an anode and $LiCoO_2$ as a cathode. This type of cell has definitively cycled Li metal thousands of times at 25°C while blocking Li shorting. Current densities across the interfaces between the electrodes can exceed 1 mA/cm^2 while achieving thousands of cycles.[1] Full-cell impedance[2] is <200 Ohm-cm^2 even with the use of planar rather than porous electrodes. These results clearly show that solid-solid interfaces can be built with low impedance and sustain current densities of 1 mA/cm^2 over thousands of cycles without significant degradation for both a Li metal/LiPON interface and a LiPON/$LiCoO_2$ interface. Unfortunately, the low ionic conductivity of LiPON means that it is deployed exclusively as a thin film.[2, 3] In this cell the cathode is also vapor deposited and is also limited to only a few microns in thickness due to Li and electron transport limitations. This results in batteries with low areal capacity (~0.2 mAh/cm^2) and low energy density, and the high fraction of inactive to active material contributes to a high cost. In short, LiPON exhibits tremendous performance in some respects (in particular, it enables the use of Li metal in cells with low areal capacity), while preventing its use in devices with relevance for large-scale energy applications.

As a second example, the class of Li garnet materials (*e.g.*, $Li_7La_3Zr_2O_{12}$) have a significantly higher conductivity than LiPON (up to ~1E-3 S/cm at 25°C, which at a thickness of 10 μm results in a favorable ionic ASR of as little as 1 Ohm-cm^2), and appears to be chemically stable with Li metal.[4-6] A thickness of 10 μm can be achieved with the scalable tape-casting process; tape-casting of thin ceramic layers has been shown to offer costs of <10 \$/m^2 at high production volumes, which is the approximate cost target for a solid separator that enables the use of Li metal.[7, 8] However, a significant number of challenges remain for Li garnet materials. (1) Observations of Li penetration through its polycrystalline structure means that dendrite-free cycling is not established across the range of desired current densities and areal capacities at 25°C.[9] (2) Air exposure results in surface chemistry that can significantly increase interfacial impedance, which may have a cost implication in terms of handling.[10] (3) They are essentially refractory ceramics, which requires sintering at ~1,000°C where Li may become volatile, making precise compositional control difficult.[11]

The third example shown in Figure 1 is LGPS ($Li_{10}GeP_2S_{12}$). LGPS is a crystalline material that represents a breakthrough in terms of the Li^+ conductivity that can be achieved with a solid material at 25°C.[12] The conductivity of LGPS at 25°C (~1E-2 S/cm, which for a thickness of 10 μm gives an ionic ASR of just 0.1 Ohm-cm^2) exceeds that of the typical liquid electrolytes used in Li-ion batteries, and because it is a single ion conductor it will eliminate concentration polarization. Unfortunately, just as sulfides typically have higher Li^+ conductivity than oxides due to the more polarizable nature of sulfur than oxygen, the sulfides typically have significantly lower chemical stability, including against Li metal and common cathode materials.[4] The reduced stability also has implications for processing, as the sulfides generally have poor air and moisture

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[2] Full-cell impedance is the resistance to current flow between two electrodes and therefore includes both ionic and electronic resistances.

stability. On the other hand, the sulfides do not require high-temperature sintering like the oxides, opening the possibility of lowering processing costs with the use of low-temperature consolidation. The shear modulus of many sulfide materials is on the order of 10 GPa, which according to theoretical predictions should be sufficient to block Li metal shorting, but as yet there is no definitive evidence that the prevention of shorting is possible.[13, 14]

These three examples of inorganic solid Li+ conductors highlight the coupled nature of key properties, including (electro)chemical stability, conductivity, processing, mechanical properties, and implications for other device components. These tradeoffs and linkages arise from fundamental principles of chemistry and physics, and the IONICS program seeks innovative approaches that can overcome such tradeoffs *and* be translated to practice in a device context.

A second main class of solid ion conductors are polymers. One key distinction among polymer electrolytes is that some are "dry," which means they are composed only of a polymer and a salt (*e.g.*, LiTFSI in PEO), while others are "wet" and contain small molecules (*e.g.*, H_2O) that are required for the ionic conduction mechanism.[15] Both "dry" and "wet" ion-conducting polymers are within the scope of the IONICS program. Two examples of hydrated polymers, rated for their performance in a fuel cell device, are shown in Figure 2.
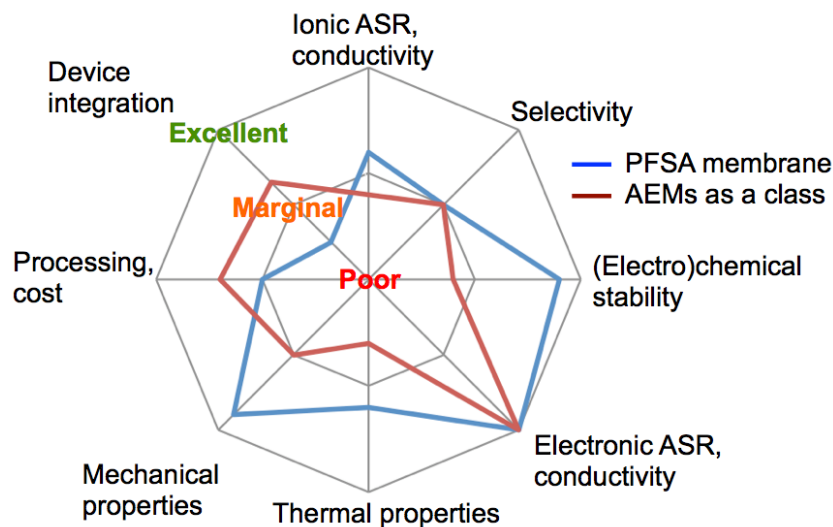

Figure 2: Radar diagram showing the qualitative attributes of two hydrated polymer ion conductors for fuel cell applications, a PFSA membrane and alkaline-exchange membranes (AEMs) taken as a class.

The first polymer example is a PFSA membrane (the word "membrane" is often used to refer to polymer and ceramic separators), discovered by Walther Grot of DuPont in the late 1960s and elaborated on by many in the years since. PFSA membranes are commercially deployed for proton-exchange membrane (PEM) fuel cells, chlor-akali production, electrolyzers, and flow batteries due to their high ionic conductivity, excellent reductive and oxidative stability and good mechanical properties. While PFSA membranes have enabled the commercial deployment of numerous electrochemical devices, some of its properties have hindered the degree of commercial uptake. In particular, the acidic nature of PFSA means that platinum group metals (PGM) are the only catalysts that can provide stable and commercially relevant rates at the oxygen and fuel electrodes at <100°C, which introduces a significant cost burden to fuel cells and electrolyzers. Efforts are underway to reduce or even eliminate the need for PGMs, but have not yet reached desired loadings while meeting other requirements such as durability.[16] Another challenge introduced by PFSA membranes is that significant hydration is required to achieve high conductivity, but is difficult to retain at high temperatures (especially above 80°C) and in direct contact with dry air or other gases. Current production of PFSA membranes for fuel cell vehicles (corresponding to sales of a few thousand vehicles per year) results in a cost of several hundred dollars per square meter.[17] In summary, PFSA membranes are the exemplar polymer solid ion conductor, with excellent chemical stability and conductivity (when hydrated), and can be easily handled and integrated in a device. However, those attributes come with a high cost (at low production volumes) and impose significant requirements for the other materials in the device (*e.g.*, the use of PGM catalysts).

The second example shown in Figure 2 is alkaline-exchange membranes (AEMs) as a class (*i.e.*, the performance values shown are typical of leading AEM membranes). A wide range of chemistries has been explored; an example composition includes a polysulfone backbone with a quaternary ammonium head group.[18-20] The main benefit of an alkaline- rather than proton-exchange membrane is that alkaline creates a path for the use of non-PGM (and hence less expensive) catalysts and uncoated, inexpensive stainless steel bipolar plates. However, AEMs generally have much lower chemical stability and moderately lower conductivity than PFSA membranes such as Nafion®. The chemical stability is lower than PFSA membranes because the high chemical stability imparted by the use of strongly electron-withdrawing fluorine in acid has not been matched by structures resistant to attack by strongly nucleophilic hydroxide anion, especially in partially hydrated states when the hydroxide anion may not be fully solvated. The need to achieve high chemical stability in a material that includes cations and is subjected to strong base is a challenge for AEMs that needs to be overcome. At the same time, an AEM also needs to resist other modes of degradation, such as that caused by radicals generated by electrode reactions. AEMs often have more swelling than PFSA membranes because the high ion exchange capacity needed to boost ionic conductivity also results in more water uptake. However, recent results have shown that AEMs, on an ion-exchange-capacity normalized basis, can reach the same conductivity as PFSA membranes under certain conditions.[21] In short, AEMs offer a path to lower cost currently inaccessible for PFSA membranes, but have performance that needs significant improvement.

From the point of view of processing and handling, polymers as a class of materials are nearly ideal because of their mechanical flexibility and ease of manufacture. Unfortunately, the engineering of polymers across all the length scales necessary to achieve low ionic resistance in a component is generally more difficult than with inorganic materials, as the >100x higher Li$^+$ conductivity at 25°C of the best inorganic materials compared to dry polymers shows.[12] While the inclusion of small molecules that facilitate conduction in polymers can dramatically improve conductivity, managing the balance of those small molecules imposes significant burdens on the overall device. Inorganic ion-conductors as a class of materials are generally more difficult to process (often requiring high temperatures where key components – such as Li – may be volatilized) and generally have mechanical properties far inferior to polymers, especially in terms of the critical property of fracture toughness. Unlike polymers (consider the ubiquitous plastic bag!), there are no widely available, free-standing, sub-50 micron inorganic layers, let alone any that can be produced for <1 $/m^2.

The examples discussed in this section were chosen to illustrate the challenges associated with the full and simultaneous realization of eight key properties required to significantly advance solid ion conductor use in electrochemical devices. There are numerous classes of materials under development as solid ion conductors not mentioned above, including metal-organic frameworks,[22, 23] covalent organic frameworks,[24] 2D materials,[25] plastic crystals,[26] and others. The IONICS program is open to any and all solid materials classes that can achieve the pertinent technical targets provided in Section I.E of the FOA.

C. PROGRAM OBJECTIVES

The overall objective of the IONICS program is to enable widespread deployment of transformational electrochemical cells with energy applications through the development of separators and porous electrodes built with solid ion conductors. To meet this objective, the IONICS program seeks to overcome difficult technical challenges associated with simultaneously achieving a wide set of property attributes, cost-effective and scalable processing of solid ion conductors, and the integration of component with solid ion conductors into devices. Building on the discussion of Figure 1 and Figure 2, Figure 3 shows a radar plot of numerous attributes of interest and the IONICS program goal of transforming components and materials from a state of limited attributes (shown in red) to a state of complete attributes (shown in green).
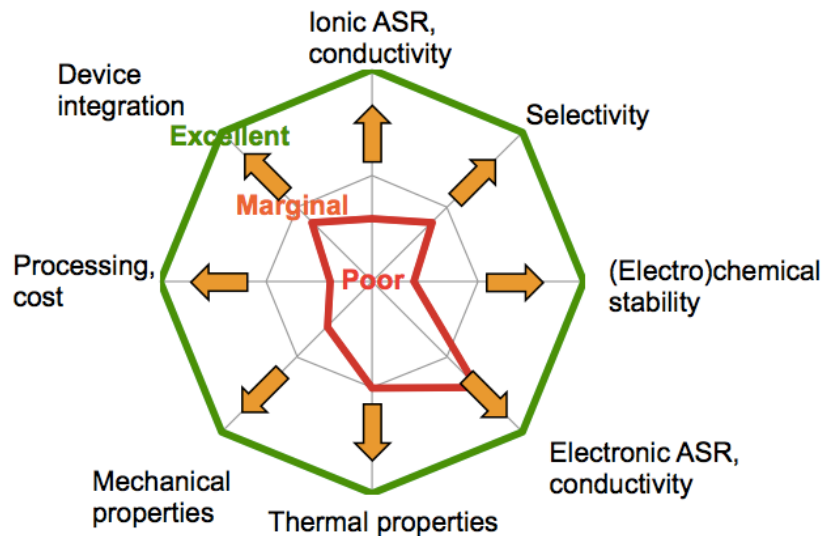
Figure 3: Radar diagram showing the overall objective of the IONICS program: replace today's components based on solid ion conductors that have limited and uneven attributes (red) with new components optimized along all the required axes (green).

As discussed in Section I.B of the FOA, the motivation behind Categories 1, 2 and 3 of the IONICS program is to develop components that can significantly accelerate the commercial potential of specific types of electrochemical cells. The motivation behind Category 4 is to allow for the development of components that will accelerate the commercial potential of electrochemical cells not specified in Categories 1, 2, or 3 and further the Program Objectives. An additional goal of the IONICS program is to establish a research paradigm in which subject matter experts from numerous backgrounds and disciplines are united by the common theme of overcoming the difficult technical challenges associated with ion-conducting solid material properties, the processing of ion-conducting solids, and the integration of ion-conducting solids into devices. Research on solid ion conductors is often conducted with a focus on only one or two properties, with ionic conductivity being the most prominent. Fully and simultaneously achieving desired property values in *every one* of the desired property values is a tremendous challenge, and in practice the device context and other constraints result in prioritization. The IONICS program seeks to confront this challenge directly, with the expectation that pursuing all desired properties simultaneously will yield new approaches that enhance performance and accelerate commercialization. While the projects in the IONICS program will work on a diverse set of materials and devices, ARPA-E anticipates productive technical exchanges among program participants along common technical themes that may include, but are not limited to, polymer/inorganic composites, chemistries that realize high stability, processing methods for large-area and thin inorganic solid ion conductors, polymer and polymer composite morphology engineering, self-forming mechanisms, and others. Specific research and development communities that ARPA-E anticipates could contribute to the IONICS program include solid state ionics, polymers, ceramics, material mechanics (especially at interfaces), functional glasses, organic and inorganic chemistry, computational approaches across a range of length scales (including approaches consistent with the Materials Genome Initiative), and process engineering and scale up.

An additional program-level objective is the creation of components with dimensions comparable to that used in a practical device. Creating components with an area matching that of relevant devices will ensure that IONICS projects will address technical challenges in moving beyond coin or button cells (with areas <10 cm^2) to areas of tens to one hundred square centimeters.

D. TECHNICAL CATEGORIES OF INTEREST

The IONICS program contains four Categories. These Categories were chosen based on an analysis of potential impact on the overall US energy sector, variety and significance of technical opportunities, and overall funding context. Each submission to the IONICS FOA must address only one of the four Technical Categories of Interest.

CATEGORY 1: LI ION CONDUCTORS THAT ENABLE THE CYCLING OF LI METAL WITHOUT SHORTING

Motivation and Impact

Li-ion batteries are currently in a phase of massive commercial adoption and manufacturing scale-up that will lower costs and catalyze the growth of electrical energy storage in both vehicle and stationary applications. However, the Li-ion technology being scaled up today has a trifecta of performance limitations that incremental progress cannot address: (1) the energy density is limited by the amount of charge that can be practically stored *via* the intercalation mechanism, (2) thermally-activated degradation modes limit the upper operating temperature to ~ 50 °C and require cooling systems, and (3) the use of organic carbonates in the electrolyte results in cells with intrinsic flammability concerns. These performance limitations have a high potential to be addressed by replacing the negative electrode with Li metal, and the liquid electrolytes in the separator and the porous positive electrode with solid ion conductors. Overcoming this trifecta of performance limitations opens a path to cell costs below 100 $/kWh and pack costs below 175 $/kWh, which would surpass the approximate limits of present Li-ion technology at large scale.[27, 28] Cost reductions at the cell level will come primarily through increasing energy density and thereby reducing the bill of materials per unit of energy stored, while improvements in thermal stability and safety will have significant benefits at the system level by reducing packaging and controls and creating design flexibility.

In the US today, about 4% of new light-duty vehicles contain a partially or fully electrified powertrain. Further improvements to batteries are widely recognized as a key barrier to wider adoption. A 10% increase in electrified powertrains will reduce US oil consumption by 3%, total US energy use by 1%, and total US CO_2 emissions by 1% (as well as reduce emissions of NO_x and other combustion products).[3] In addition to impacts on vehicles, cell technology that is energy dense, thermally stable, and non-flammable will be of interest for grid storage, particularly in dense urban environments.

Technical Opportunities

The minimum requirement for Category 1 is to definitively show the cycling of Li metal at conditions defined in Section I.D of the FOA. Cycling of Li metal without shorting at 25°C has been a goal in the battery community for decades, however it has been successfully proven only in thin-film cells based on LiPON solid electrolyte with low areal capacity, which creates serious limitations as discussed in the context of Figure 1. While an understanding of the fundamental ingredients required to cycle Li metal continues to mature, an important theoretical paradigm (with some empirical support) is that a separator material with a shear modulus approximately twice that of Li metal itself is sufficient to block dendrites.[14, 31] LiPON far exceeds this threshold, although it should be noted that some solid electrolytes (*e.g.*, the Garnet material discussed in the context of Figure 1) do allow Li penetration through grain boundaries even though they have a sufficient shear modulus.[9, 13, 32] Recent years have seen tremendous developments in the area of Li-conducting solid phases; especially noteworthy is the 2011 report of $Li_{10}GeP_2S_{12}$ (LGPS) that has an ionic conductivity greater than typical commercial Li-ion electrolytes.[12] Sn and Si versions of that material have also been prepared that have roughly equivalent conductivity to the Ge version.[33, 34] There have also been significant advances in Li-conducting ceramic oxides, glasses, and polymers. Although no single material today has all of the desired properties shown in Figure 1, each desired property can be found among the entire set of Li+-conducting materials. This naturally leads to the idea that the desired set of properties may be achieved with composites of existing materials. Engineering the interfaces among the various phases to ensure that low ionic resistance, mechanical properties sufficient to block Li metal shorting, thermal stability, *etc.*, are realized *at the component level* is a critical technical path for the composite approach. Recent results by IBM research for a Li-conducting ceramic in a polymer matrix is an example of this approach.[35] While the minimum requirement of Category 1 is to cycle Li metal according to the metrics defined in Section I.E of the FOA, proposals may also include the construction of porous electrodes built from solid Li+-conducting materials. The emphasis of work on porous electrodes should be on approaches that can successfully integrate solid Li+ conductors with solid active materials and other components to impart thermal stability and safety characteristics unattainable with Li-ion technology.

Examples of technical approaches of interest for Category 1 include, but are not limited to:

- Composites of existing Li+ conducting materials, especially polymer/ceramic composites with a high potential to achieve both a full set of desired properties and an ability to use existing roll-to-roll processing lines.[35]

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[3] Electric drivetrains includes hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV), and full battery electric vehicles (BEV). Calculation assumes electric drivetrain vehicles will be sold in a 2:1:1 ratio (HEV:PHEV:BEV).[29] Reductions are based on a "well-to-wheels" analysis which evaluates feedstock production, processing, fuel production, fuel delivery, as well as vehicle energy use.[30]

- Composites of existing Li+ conducting materials inspired by successful composites of other ion-conducting materials.[36]
- Low-cost, continuous, scalable processing techniques for inorganic solid ion conductors. As one example, a process is under development to make thin (down to 20 microns), flexible, polycrystalline, ceramic layers.[37]
- New materials that offer significantly improved properties compared with existing materials. As one example, a dry Li+-conducting polymer that achieves a conductivity exceeding 5E-4 S/cm at 25°C and other desired properties would be a significant advance.
- The use of self-forming mechanisms to create passivating interfacial layers, or even the active materials or the separator itself, as a way to reduce processing steps.[38, 39]
- Supported films, which allow ion conductor thickness significantly less than 20 microns.

Note: All technology examples provided in this FOA are only meant to illustrate principles, and they are not meant to prescribe or limit the technical approaches proposed under the IONICS program.

Areas specifically NOT of interest in Category 1 are described in Section III.C.3 of the FOA.

CATEGORY 2: SELECTIVE AND LOW-COST SEPARATORS FOR BATTERIES WITH LIQUID REACTANTS (E.G., FLOW BATTERIES)

Motivation and Impact

The cost of electricity from wind and solar is increasingly favorable for mass deployment. Unfortunately, the limitations of the present electric power grid can prevent integration of abundant, but intermittent, wind and solar resources to as little as ~20% (the number varies with location and other factors) of the energy on the grid without significant curtailment.[40] More secure, reliable, and flexible operation of the grid can be accomplished through grid expansion (averaging over larger areas to reduce variability), responsive load, energy storage, or ramping of assets such as gas turbines (the current practice). Category 2 of the IONICS program is focused on energy storage, where ARPA-E's goal is to develop a transformative approach that allows the delivery of wind and solar energy with "firm" capacity near US wholesale prices. This requires adding only a few cents per kWh to wind and solar prices, which roughly corresponds to a *fully installed capital cost* (on an AC/AC basis) of 150 $/kWh, assuming at least 5,000 cycles and 80% round-trip efficiency. A system with these attributes would profoundly transform electricity systems around the world and pave the way for significantly more integration of wind and solar, especially at deep penetration levels (>50%). Past efforts funded by ARPA-E (including the GRIDS program and many projects in the OPEN portfolios) have developed advanced technologies in pursuit of this goal. The IONICS program is aimed at key issues identified in previous research and development efforts on energy storage for the grid, with a specific focus on separators for batteries with liquid reactants.

Batteries that use liquid reactants have a high potential to achieve extremely long cycle life because they avoid the numerous degradation modes associated with solid reactants, including those present in Li-ion batteries that often limit cycle life to 1,000 cycles or less. Cost modeling for aqueous liquid reactant batteries has established a challenging, but plausible, path to *fully installed systems* at 150 $/kWh for a five hour discharge time, a cost point that Li-ion batteries are not expected to reach.[41] These liquid reactants are typically embodied in a flow cell design, in which liquid reactants are stored in tanks and pumped to a stack of cells in which power is produced and accepted.[42] A significant advantage of flow batteries is the ability to decouple the energy and power portions of the battery, allowing the power portion to be specifically designed for highest performance and lowest cost. Flow batteries are particularly advantageous for long discharge times (*i.e.*, ≥5 hours). Other liquid reactants also have potential for extremely long cycle life and low cost; the most prominent examples make use of liquid sodium metal (or a sodium alloy) and a solid Na+-conducting separator in a non-flow arrangement.[43-45]

The fundamental challenge with the use of liquid reactants is that realizing their promise of high cycle life can be accomplished in only two ways: (1) use a separator with essentially perfect selectivity for a common ion that passes between the electrodes (*e.g.*, a solid Na+-conducting solid electrolytes such as β''-Al$_2$O$_3$), or (2) find a liquid reactant for which crossover does not lead to permanent cell degradation but only a loss in efficiency. The challenge in case (1) is that a "perfectly" selective separator has not yet enabled a low-cost system (*c.f.*, the Na/S battery, with reactants costing <1 $/kWh, nevertheless costs far more than 150 $/kWh at the system level), in part because of the cost of such a "perfect" separator. The challenge in case (2) is that there is only one practical example, to date, of a reactant that can be renewed when it crosses through the separator. That case is vanadium, which is cycled in its 2/3 and 4/5 oxidation states (at the negative and positive electrodes, respectively); these oxidation states have an adequate potential difference (a 1.25 V standard cell potential) and are suitability located relative to the stability window of aqueous electrolytes. Unfortunately, the vanadium

itself costs between 35 and 85 $/kWh (the price in the past fifteen years has largely depended on demand in the steel industry), preventing flow cells built with vanadium reactants from reaching ≤150 $/kWh for fully installed systems.[41] Further, even the vanadium system requires the use of an ion-exchange membrane to limit crossover, and available PFSA membranes add 25 $/kWh or more (for a 5 hour discharge time) to the system cost.

Technical Opportunities

There are two basic directions to drive advances in separators for batteries with liquid reactants: (1) Develop a high-performance separator with essentially perfect selectivity that creates two separate compartments coupled only by the exchange of a desired ion or ions. This approach offers tremendous design flexibility because it can fundamentally decouple the conditions at the two electrodes. (2) Develop separators for liquid reactants that do not require "perfect" selectivity and decoupling of the electrodes, but where achieving a lower cost than PFSA membranes *at near-term production volumes* would significantly hasten market adoption.[4] Crossover that leads to irreversible degradation (Case (1)) requires a per-cycle selectivity[5] in excess of 99.995% to achieve 5,000 cycles while retaining 80% of the initial capacity. Inorganic materials have the potential to reach such a high selectivity because of their highly selective ion-conducting channels, but ion-conducting inorganic materials are typically expensive and require high operating temperatures to achieve high-efficiency cell operation. For case (2), there are a number of engineered liquid reactants under development that often make use of PFSA membranes because of their ready availability, but would greatly benefit from the development of membranes with superior performance-to-cost ratios, especially at the low production volumes facing flow battery manufacturers in the emerging grid storage market. PFSA membranes have anion-lined conducting channels with a characteristic size of 2-3 nm, sufficient for many reactants such as vanadium to achieve >97% selectivity during cycling, an adequate value for overall system operation.[41, 46-48] The design of ion-conducting channels in separators that are specifically tailored to the conditions present with emerging reactants based on Fe, Cr, S, quinones, *etc.*, is a key goal for Category 2. [49-51] Although the primary focus of Category 2 is the creation of selective membranes that further the development of low-cost batteries with liquid reactants, membrane design is often inextricably connected with the nature of the liquid reactants and so Category 2 is open to funding the co-development of membranes *and* liquid reactants. Several recent ideas show promise for creating separators with high selectivity and other performance attributes, and constitute examples of technical approaches of interest in Category 2.

Examples of technical approaches of interest for Category 2 include, but are not limited to:

- Inorganic nanoparticles blended into a porous polymer membrane that can fill pores and help block large active ions. [52]
- Both anion exchange membranes and amphoteric (possessing both acid and base character) polymers have shown promise in reducing the crossover of positively charged active species without significantly affecting conductivity.[53-55]
- Designing active species to have physically large cross sections and then combining them with a nanoporous membrane that may be infiltrated with an ionomer[50, 56] potentially allows for both high selectivity (*via* a combination of size and charge exclusion) and low resistance (*via* the small thickness of the supported membrane).
- Thin layers of inorganic materials may offer extremely high selectivities and low resistance even at 25°C, especially with the use of very thin, supported inorganic layers. Such an approach would need to meet the challenge to devise a fabrication technique with sufficiently low cost necessary for widespread implementation.[37, 57, 58]
- Separators enabling the use of molten sodium or sodium alloys at temperatures near 100°C and below.[44, 45]

Note: All technology examples provided in this FOA are only meant to illustrate principles, and they are not meant to prescribe or limit the technical approaches proposed under the IONICS program.

Areas specifically NOT of interest in Category 2 are described in Section III.C.3 of the FOA.

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[4] Section I.D of the FOA defines cost targets and production volumes.

[5] The definition of selectivity for the purpose of Category 2 is the following: (number of moles of desired ion passed over a full charge/discharge cycle) / (number of moles of desired ion passed *plus* the number of moles of reactant or other species that lead to degradation or a loss of current efficiency per charge/discharge cycle).

CATEGORY 3: ALKALINE CONDUCTORS WITH HIGH CHEMICAL STABILITY AND CONDUCTIVITY

Motivation and Impact

Despite a number of drawbacks, hydrogen remains a compelling energy carrier because of its abundance, ease of synthesis, point-of-use emission of only water, usefulness as a fuel or in chemical processes, and other benefits. Vehicles that use proton-exchange membrane fuel cells (PEMFCs) are available for sale (*e.g.*, the Toyota Mirai), and numerous applications for hydrogen fuel cells and electrolyzers have been identified.[59, 60] A particular advantage for hydrogen as fuel carrier, compared with batteries, is the ability to fully charge a vehicle with a 300-mile range in minutes, similar to existing gasoline vehicles. A future with hydrogen as a significant energy carrier depends, to a significant degree, on advances in the oxygen electrode. The oxygen electrode has been explored in many reaction media (*e.g.*, aqueous media across a broad range of pH values, as well as nonaqueous and solid ceramic), but has been most heavily developed at acidic pH for automotive hydrogen fuel cells. The reason for the pursuit of the acid pathway is the existence of PFSA membranes, discussed earlier in the context of Figure 2. A consequence of the operation of the oxygen electrode in acid media is the need to use PGMs as a catalyst, as well as carbon-based or coated metal bipolar plates. Significant efforts are underway to reduce the amount of PGMs required, including efforts to develop viable non-PGM catalysts.[61, 62] While state-of-the-art Pt loadings of 0.15 mg/cm^2 have been achieved for automotive applications, commercial loadings (*e.g.*, as estimated for the Toyota Mirai) are typically ~0.3 mg/cm^2 or higher due to reliability concerns, translating into ~30 g of Pt per vehicle.[63] At this loading an annual production of ~7 million vehicles would require doubling of the current annual production of Pt. At a Pt price of 1500 \$/troy ounce, at high production volumes (500k vehicles/y) the cost of Pt accounts for 49% of the total stack cost.[17] In addition, an acid system requires the use of a coating on the surface of stainless steel bipolar plates, resulting in plates that account for 22% of total stack costs.[17] Taken together, the cost of these two components significantly hinders the ability of PEMFC systems to achieve their ultimate cost targets.[16]

As an alternative, the oxygen electrode can operate in basic media with non-noble catalysts such as Ni and uncoated stainless steel bipolar plates.[19] Indeed, alkaline electrolyzers and fuel cells have been deployed for terrestrial and space applications with liquid alkaline electrolytes. But there are major drawbacks for both fuel cells and electrolyzers with a porous separator running on liquid alkaline electrolytes: for fuel cells, strongly basic liquid electrolytes react with CO_2 in air and form carbonate precipitates that degrade performance, requiring the use of pure O_2. For electrolyzers, compressed hydrogen is typically desired, but a porous separator with a liquid electrolyte cannot sustain the pressure differentials of a solid polymer (*cf.*, PFSA membranes can be designed to withstand pressure differentials of hundreds of bar).[64] The use of an AEM with cationic head groups bonded to a backbone can potentially resolve both of these challenges and enable the promise of operating the oxygen electrode in base in a practical system. In particular, an AEM can prevent carbonate precipitation upon air exposure (although AEM conductivity is reduced in the carbonate form compared to the hydroxide form) and sustain a pressure gradient to grant the benefits of electrochemical hydrogen compression. Overall, cost estimates of an AEM stack show a potential for ~25% lower system cost than using a PEM stack, and this CapEx benefit is roughly the same for automotive and combined heat and power (CHP) fuel cells.[6]

In short, the development of a high-performance alkaline-exchange membrane has a high potential to put the oxygen electrode, as embodied in fuel cells for automotive or stationary applications as well as electrolyzers, on a fundamentally lower cost trajectory.

Technical Opportunities

No alkaline-exchange membrane is currently available with properties comparable to PFSA membranes. The biggest challenge for AEMs at present is achieving a high chemical stability at desired operating temperatures of ≥80°C, and ideally ≥95°C. Achieving these temperatures is critically important because they allow for cost-effective and compact heat rejection.[7] For fuel cell applications where air is a reactant, good conductivity must be achieved with bicarbonate and

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[6] For proton exchange membrane (PEM) fuel cells, the platinum-based catalyst and bipolar plates constitute over 70% of the fuel cell stack costs at high volumes.[17] By moving to an alkaline environment stack costs can potentially be reduced by 50%, resulting in vehicle fuel cell system cost reductions of up to 25%. Assumptions: use of non-PGM based catalysts and enablement of uncoated steel bipolar plates due to the reduced corrosion in the alkaline environment. Stack costs constitute 50% of system level costs for high volume PEM fuel cell production models.[17]

[7] For example, the Department of Energy has set a target for $Q/\Delta T$, the heat rejection rate (Q) over the available temperature difference (ΔT) between a fuel cell temperature and a defined ambient temperature.[65]

carbonate from CO_2, and operation in a partially hydrated state is also necessary. A wide range of chemistries is being pursued, with backbones typically drawn from among the set of polymers that are stable in strong alkaline solutions at high temperatures, such as poly(arylene ethers), poly(ether ether ketone), poly(ether-imide), and various fluoropolymers.[19, 66, 67] Numerous tethers and cation head groups are also under exploration; benzyl- and alkyl-substituted quaternary ammonium groups are the most common cation head groups. In general, the resulting membranes exhibit stability for up to thousands of hours at ≤60°C and have conductivity moderately lower than PFSA membranes.[20]

There are a number of promising new chemistries emerging as well as a set of approaches to engineer the morphology of AEMs that have not yet been thoroughly explored.[68-70] Among the promising new chemistries, AEMS with high conductivity (>100 mS/cm at 80°C), stability in strong base at 80°C for several weeks, and good mechanical properties have been established, although achieving all of these property values in a single material, and showing they can be retained across a range of hydration levels and with an acceptable degree of swelling for device integration, has not been proven.[71-76] In terms of morphology engineering, the idea is to create segregated regions of hydrophobic and hydrophilic channels. Such a structure decreases the interaction between the hydroxide groups and the polymer backbone and has shown the potential to dramatically reduce degradation.[21, 77, 78] Morphology engineering may also help overcome classic tradeoffs among, for example, ionic conductivity and mechanical strength due to competing dependencies on swelling of ionic sites.[21, 79] Inorganic/organic composite membranes are another approach that shows promise for creating conductive and stable AEMs.[80]

Examples of technical approaches of interest for Category 3 include, but are not limited to:

- Approaches that retain the compelling performance that has been shown for a subset of properties while realizing significantly improved performance in all other properties.
- Morphology engineering to create phase-segregated structures that simultaneously address chemical stability, conductivity, mechanical properties, and other attributes relevant to AEM performance.
- Inorganic/organic composite membranes.
- AEMs capable of operation at temperatures significantly above 80°C, which is beneficial for heat transfer out of fuel cell systems.
- Material compositions and processing techniques that enable low cost at low production volumes.

Note: All technology examples provided in this FOA are only meant to illustrate principles, and they are not meant to prescribe or limit the technical approaches proposed under the IONICS program.

Areas specifically NOT of interest in Category 3 are described in Section III.C.3 of the FOA.

CATEGORY 4: OTHER APPROACHES THAT COULD ACHIEVE THE IONICS PROGRAM OBJECTIVES

This Category supports the development of components built with solid ion conductors that fall within the overall vision of the IONICS program but do not fit within Categories 1 to 3. In particular, Category 4 targets transformative electrochemical cells for the energy sector that are limited by a component that could be significantly improved with a solid ion conductor. The goal for this Category, as for the other Categories, is to achieve a technical breakthrough and a practical demonstration at the component level. While the purpose of this Category is to be open to high-impact innovations outside of Categories 1 to 3, applicants should be aware that there is a higher burden to quantify the potential impact of innovations.

Examples of technical approaches of interest for Category 4 include, but are not limited to:

- Solid ion conductors that enable the production of light metals such as Al and Mg in electrolytic cells. Highly stable metal oxide conductors are of interest, as are materials that directly conduct Mg^{2+} or Al^{3+} to allow the direct production of purified metal at the cathode.
- Low-cost separation of the components of air, especially at scales smaller than cryogenic processes, is important for applications such as oxy-combustion and the production of ammonia. Solid ion conductors that create new learning curves for the separation of the components of air are of interest.

Note: All technology examples provided in this FOA are only meant to illustrate principles, and they are not meant to prescribe or limit the technical approaches proposed under the IONICS program.

Areas specifically NOT of interest in Category 4 are described in Section III.C.3 of the FOA.

E. TECHNICAL PERFORMANCE TARGETS

The IONICS program is focused on transformative components built from solid ion conductors, and the technical performance targets in this section are focused at the component level. Component testing in devices to verify component performance is required for particular Categories, as further described below.

Proposed technical plans must show a well-justified potential to meet or exceed the quantitative Technical Performance Targets described below.

CATEGORY 1: LI ION CONDUCTORS THAT ENABLE THE CYCLING OF LI METAL WITHOUT SHORTING

Technical Metrics
The following metrics apply to solid Li^+-conducting separators, the minimum requirement of Category 1:

ID	Metric	Value
1.1	Separator that enables the cycling of Li metal without shorting at 25°C[A]	Modulus, surface, and microstructural properties that prevent Li metal shorting
1.2	Thermal properties[B]	Suitable for cell operation from −20 to 70°C
1.3	Component area over which property values are achieved to within ≥90% uniformity[C]	≥30 cm^2
1.4	Cost[D]	≤$10/m^2
1.5	Ionic ASR at 25°C	≤5 Ohm-cm^2
1.6	Capacity of Li metal moved per cycle	≥3 mAh/cm^2
1.7	Current density	≥3 mA/cm^2
1.8	Number of cycles without Li metal shorting, or ≥20% degradation of other performance metrics	≥500
1.9	Electrochemical stability[E]	0-4.5 V *vs.* Li/Li$^+$ is desired; sufficient to meet metric 1.14 is required
1.10	Thickness	≤20 µm
1.11	Depth of discharge of the Li electrode (*i.e.,* fraction of the Li metal present that is cycled)	≥80%
1.12	Electronic ASR at 25°C	≥1E5 Ohm-cm^2
1.13	Mechanical properties for handling and operation	Suitable for handling components with an area at least that defined in metric 1.3, and for operation
1.14	Device Integration	Suitable for integration into a cell that achieves ≥1000 Wh/L and ≥400 Wh/kg for the cell repeat unit (current collectors, electrodes, and separator)

[A] At present, theoretical and empirical results suggest that a shear modulus approximately twice that of Li metal itself is required to prevent Li shorting.[14, 31] Proposals for solid separators with a significantly lower modulus should provide theoretical and/or empirical rationale for why they will be able to block Li metal shorting.

Thermal properties need to be sufficient such that a cell built with this separator can operate without external heating or cooling across a wide range of ambient temperatures relevant for automotive or outdoor use. At low temperatures this means the conductivity is sufficiently high that the cell can self-heat, and the mechanical properties are such that Li metal shorting is still avoided, albeit at a lower current density than higher temperatures. At high temperatures this means the cell can operate without unacceptable degradation.

[C] Component development and testing work, including *in situ* device testing, may be done on areas smaller than that defined in metric 1.3, but a scientifically principled approach to scale-up must be developed and components with the area in metric 1.3 must be made and tested by the end of the program.

[D] At a battery production capacity of 10 GWh per year. This cost target is estimated with the following assumptions: a separator cost to energy of <20 \$/kWh, a discharge time of 3h, and a power density of 10 mW/cm^2. See reference [8] for a relevant cost discussion.

[E] Accurate measurements of electrochemical stability are not simple. Two comments: (1) Measurements of electrochemical stability with cyclic voltammetry are generally inadequate for device-relevant stability. An important objective of the IONICS program is to significantly raise the bar on measurements of the electrochemical stability of solid Li$^+$ conductors. (2) A true thermodynamic stability window of 4.5V is not expected; rather, kinetic stability imparted through the formation of stabilizing, interfacial layers is expected to provide stabilization.

As stated previously, proposals to Category 1, in addition to the minimum requirement of enabling the cycling of Li metal with metrics 1.1 to 1.14, may also propose the construction of porous electrodes built from solid Li$^+$-conducting materials, in which case metrics 1.15 to 1.23 also apply.

ID	Metric	Value
1.15	Component area over which property values are achieved to within ≥90% uniformity[F]	≥30 cm^2
1.16	Thermal properties[G]	Suitable for cell operation from −20 to 70°C
1.17	Ionic conductivity of conducting phase	≥5E-4 S/cm
1.18	Electrode-level ASR measured at 50% SOC under practical compression conditions[H]	≤50 Ohm-cm^2
1.19	Electrode capacity	≥3 mAh/cm^2
1.20	Number of cycles with 80% capacity retention in a full-cell format at ≥1 mA/cm^2	≥500
1.21	Electrochemical stability	Suitable for use with positive electrode materials that enable metric 1.14
1.22	Mechanical properties of composite electrode	Suitable for cell manufacturing process that enables cells at 100 \$/kWh (*i.e.*, suitable for roll to roll processing is preferred)
1.23	Device integration	The creation of a solid-state cathode based on existing metal-oxide electrode materials is preferred; other electrode materials will be considered on a case-by-case basis

[F] Component development and testing work, including *in situ* device testing, may be done on areas smaller than that defined in metric 1.15, but a scientifically principled approach to scale-up must be developed and components with the area in metric 1.15 must be made and tested by the end of the project.

[G] See note for metric 1.2 above.

[H] A common method to maintain interfacial contact in solid state electrodes is to apply high pressures. Metric 1.16 must be measured at pressures that can be practically achieved in a battery pack.

Project Deliverables

The final project deliverables for Category 1 are:

- For projects exclusively addressing metrics 1.1 to 1.14, both symmetric cell (Li metal *vs.* Li metal) testing and full cell (Li metal *vs.* a cathode) testing are required. Full cell testing may be done with a conventional Li-ion cathode and liquid electrolyte to reduce complexity. Cell testing may be done at area smaller than that in metric 1.3, but cell testing at the area of metric 1.3 is required by the end of the project.
- For projects also addressing metrics 1.15 to 1.23, cells with Li metal as the negative electrode and the proposed solid porous positive electrode must be tested. Cell testing may be done at area smaller than that in metric 1.15, but cell testing at the area of metric 1.15 is required by the end of the project.

CATEGORY 2: SELECTIVE AND LOW-COST SEPARATORS FOR BATTERIES WITH LIQUID REACTANTS (E.G., FLOW BATTERIES)

Technical Metrics

ID	Metric	Value
2.1	Production cost for a battery system with liquid reactants, a 5 hour charge and discharge time, and 80% round-trip DC-DC efficiency[A,B,C]	≤100 $/kWh
2.2	Expected cycle life to 80% of initial capacity given separator selectivity	≥5,000
2.3	Component area over which property values are achieved to within ≥90% uniformity[D]	≥100 cm^2
2.4	Per-cycle selectivity when reactant crossover leads to irreversible capacity loss[E]	>99.995%
2.5	Separator cost to energy at production volume of 100 MW/y for a separator that achieves >97% selectivity [F]	≤10 $/kWh
2.6	Ionic ASR	Sufficient to provide power density to meet metric 2.1; for aqueous flow batteries, <0.3 Ohm-cm^2 as described in reference [81]
2.7	Electronic ASR	≥1E4 Ohm-cm^2
2.8	Separator electrochemical and chemical stability	≤0.4% performance degradation per 1,000 hours of cycling over potential window and electrode compositions
2.9	Mechanical properties	Sufficient for handling during device fabrication, and for stable operation over ≥5,000 cycles

[A] At a production capacity of 2 GW / 10 GWh per year (a 5 hour system).
[B] For this metric a battery system is defined to include all of the items required to provide and receive DC power, but excludes costs such as inverters, project development and siting costs, utility interconnections, *etc.* The energy basis for this calculation should be the usable energy of the system. ARPA-E refers readers to reference [41] for an excellent cost analysis and set of specific component cost targets, especially for flow batteries.
[C] Note the specification of a battery system cost target provides applicants flexibility to balance the costs of individual components. However, ARPA-E is generally looking for separator costs to energy of <10 $/kWh for the system specifications in metric 2.1.

D Component development and testing work, including *in situ* device testing, may be done on areas smaller than that defined in metric 2.3, but a scientifically principled approach to scale-up must be developed and components with the area in metric 2.3 must be made and tested by the end of the project.

E The definition of selectivity for the purpose of Category 2 is the following: (number of moles of desired ion passed over a full charge/discharge cycle) / (number of moles of desired ion passed *plus* the number of moles of reactant or other species that can lead to degradation or a loss of current efficiency per charge/discharge cycle)

F For separators that do not offer the enabling and extremely high selectivity required when crossover leads to irreversible degradation, the separator should still achieve >97% selectivity *and* provide a significantly lower cost at near-term production volumes (100 MW/y) than PFSA separators, while providing equivalent or superior performance. See Figure 57 of reference [17] for the expected cost/volume curve of a supported PFSA membrane.

Project Deliverables

The final project deliverables for Category 2 are:
- Both *ex situ* (*e.g.*, measurements of chemical stability as defined in metric 2.8 may be at least partially accomplished with an extended soak) and *in situ* (*e.g.*, measurements of expected cycle life as defined in metric 2.2) measurements are expected. Both *ex situ* and *in situ* measurements may be done with component areas smaller than that defined in metric 2.3, but a scientifically principled approach to scale-up must be developed and components with the area in metric 2.3 need to be made and tested by the end of the project. Cell testing at an area smaller than that defined in metric 2.3 is acceptable throughout the project.
- As stated in the discussion of Category 2 in Section I.C of the FOA, membrane development is often inextricably connected to the development of reactants, so projects in Category 2 may also propose to deliver reactants co-developed with selective separators.

CATEGORY 3: ALKALINE CONDUCTORS WITH HIGH CHEMICAL STABILITY AND CONDUCTIVITY

Technical Metrics

ID	Metric	Value
3.1	Membrane chemical stability (at ≥80°C immersed in a pH≥14 solution)A	≥1000 hours with ≤2% loss in ion exchange capacity, ionic ASR, spectroscopic measures of membrane state, and mechanical properties
3.2	Component area over which property values are achieved to within ≥90% uniformityB	≥100 cm^2
3.3	Ionic ASR (hydroxide form, 80°C, liquid equilibrated)	≤0.04 Ohm-cm^2
3.4	Ionic ASR (80°C, ≤50% RH, under air exposure, *i.e.*, in presence of 400 ppm CO_2)	≤0.08 Ohm-cm^2
3.5	Mechanical durability during humidity cyclingC	≥20,000 RH cycles
3.6	Electronic ASR	≥1000 Ohm-cm^2
3.7	Humidity Stability FactorD	>5
3.8	Swelling in liquid water at 25°C	<50%
3.9	Pressure differential (bar)	≥1
3.10	H_2 crossover and O_2 crossover	≤25 nmol/cm^2-s
3.11	Cost for membrane that can be practically integrated in a deviceE	≤20 $/m^2

<superscript>A</superscript> For a discussion of spectroscopic and mechanical tests that may be done to characterize degradation see [19] or [82]

<superscript>B</superscript> Component development and testing work may be done on areas smaller than that defined in metric 3.2, but a scientifically principled approach to scale-up must be developed and components with the area in metric 3.2 must be made and tested by the end of the project.

<superscript>C</superscript> The RH testing procedure is described in reference [83]. Membrane mechanical properties must be sufficiently retained during RH cycling; the most important metric for this is the membrane's ability to maintain low levels of gas crossover, as defined in metric 3.10.

<superscript>D</superscript> Definition: (Strain at breaking point at 25°C and 50% RH) / (Linear swelling at 100°C in liquid water). This metric is a rough check to ensure that a membrane can stretch more at 25°C than it naturally swells when fully hydrated at 100°C, and has been found to correlate with RH cycles to failure. See references [84] and [85] for further discussion.

<superscript>E</superscript> At a production capacity to supply 100,000 fuel cell vehicles per year. "Practically integrated" refers to the mechanical properties required for handling and device manufacturing.

Project Deliverables

Membrane testing in Category 3 will be exclusively *ex situ* because *ex situ* testing facilitates the ability to test new ideas without the significant complexity of full cell fabrication and instrumentation, especially given the Category 3 focus on AEMs stable at high temperatures.*.* ARPA-E understands the value of *in situ* testing, as well as the high importance of the development of ionomers for the electrodes, and may consider funding such work, subject to the availability of appropriated funds. Further, while there are significant differences in the requirements around hydration and applied pressure for fuel cells and electrolyzers, the single set of metrics for Category 3 is oriented towards the fuel cell application. Significant progress towards these metrics should result in membranes that can be transferred to electrolyzers for testing and further development, another potential topic for additional work under a later funding mechanism. Hence, the end-of-project deliverable for Category 3 is a set of components with an area defined by metric 3.2 that meets the other metrics in the Category 3 table above.

CATEGORY 4: OTHER APPROACHES THAT COULD ACHIEVE THE IONICS PROGRAM OBJECTIVES

Technical Metrics

This Category may encompass a range of approaches and applications. Applicants must present the technical metrics they plan to achieve during the course of their project following the format presented in the Table below. Applications proposing solid ion conductors that could be used in multiple types of electrochemical cells should clearly state the expected impact of at least one electrochemical cell containing proposed innovations, so ARPA-E can be sure that the impacts are sufficient to warrant support.

The suggested format for presentation of technical metrics for applications in Category 4 is:

ID	Metric	Value
4.1	Component area over which property values are achieved to within ≥90% uniformity	Comparable to that in relevant electrochemical device (cm^2)
4.2	Ionic area-specific resistance	Provide expected thickness in microns and ASR in units of Ohm-cm^2
4.3	Selectivity	Describe what ions and neutral species the solid ion conductor is selective towards and method to measure selectivity. Provide selectivity with units as appropriate (*e.g.*, a per-pass current efficiency, or a side reaction current density at steady state)
4.4	Electrochemical and chemical stability	Measurement technique and duration of chemical stability, with units of hours, volts, *etc.*, as appropriate

4.5	Electronic area-specific resistance	Provide expected thickness in microns and ASR in units of Ohm-cm^2
4.6	Thermal properties	Describe relevant thermal characteristics, including ASR as a function of temperature, the presence of phase changes, the temperature at which irreversible degradation mechanisms begin, *etc.* Provide thermal characteristics with relevant units, such as ASR in Ohm-cm^2 as a function of temperature, the temperature at which a degradation rate exceeds the target for the desired operating life of the device, *etc.*
4.7	Mechanical properties	Mechanical properties relevant to both function in the device and to the processing and handling steps. Examples: fracture toughness, shear modulus, tensile strength, hydration cycling, *etc.*
4.8	Processing and cost	Description of processing method and the assumed attributes and production volume in cost target. Provide cost as $/m^2 as a function of volume in m^2/year.
4.9	Device integration	Describe implications of solid ion conductors properties on other parts of the device
4.10	Impact	Components built from solid ion conductors for electrochemical devices that have a clear potential to impact at least 1% of US energy-related emissions, imports, or overall energy use.

Project Deliverables

A set of components with an area defined by metric 4.1 that meets the other metrics in the Category 4 table above. Applicants should propose a level of testing appropriate for their component.