U.S. Department of Energy
Advanced Research Projects Agency – Energy

Request for Information (RFI)
DE-FOA-0001396
on
Ion Conductors for Electrochemical Cells

Objective:

ARPA-E seeks input from researchers and technologists from a broad range of fields on how to achieve transformational gains in the ability to selectively conduct ions in electrochemical cells with significant impacts on ARPA-E mission areas. ARPA-E is particularly interested in ideas that will realize the full set of attributes required by a practical electrochemical device. In addition to ion (and optionally electron) selectivity, such attributes typically include suitable ionic and electronic conductivity, chemical and thermal stability, mechanical properties, cost-effective manufacturing and device integration, and others required by a particular application (e.g., density and thickness are of particular importance for mobile applications). ARPA-E seeks innovations that are deeply informed by the inextricable links among materials, fabrication, and the device or process context. The information you provide may be used by ARPA-E in support of program planning. THIS IS A REQUEST FOR INFORMATION ONLY. THIS NOTICE DOES NOT CONSTITUTE A FUNDING OPPORTUNITY ANNOUNCEMENT (FOA). NO FOA EXISTS AT THIS TIME.

Background:

The electrochemical cell holds great potential to couple chemical transformations with electrical energy and thereby significantly impact ARPA-E's mission areas, which include improving energy efficiency, reducing energy imports, and reducing energy-related emissions in the United States. For cases in which electrical energy provides work to produce chemicals (electrolytic processes), that electrical energy can come from low-emission primary energy sources such as solar, wind, and nuclear. Energy stored in chemicals can then be returned to electricity at a desired time (galvanic processes). Both electrolytic and galvanic processes can be carried out at high efficiency and across a wide range of scales. High efficiency and scalability are well exemplified by batteries. The Li-ion batteries deployed in electric vehicles and for grid storage can easily achieve 85% round-trip efficiency (DC-to-DC) at practical rates and are deployed as systems at scales ranging from milliwatts to megawatts. In addition to batteries for automotive and grid storage applications [1, 2], electrochemical cells are already widely deployed in areas with significant impacts on ARPA-E mission areas including those in chemical production (most notably the aluminum production and chlor-alkali processes [3]) and O_2 and NO_x sensors used in vehicle emissions control.[4] The great promise of electrochemical processes is reflected in the fact that ARPA-E has run a broad range of programs in which electrochemical cells play a major role, including BEEST (batteries), GRIDS (batteries), RANGE (batteries), METALS (light metal production), REBELS (fuel cells, including some with energy storage and electrosynthesis functionality), GENSETS (alkali metal thermal to electrical converter cells), and OPEN (gas to liquids and other cells).

An electrochemical cell is minimally composed of three components: two electrodes and a separating layer that conducts ions. In many electrochemical cells the electrodes are porous to increase interfacial reaction area and ionic conduction is therefore required in all three components. ARPA-E's electrochemical projects have generally focused on the development and demonstration of small-scale electrochemical devices, and have pursued advances in each element of the electrochemical cell. Based on ARPA-E's funding experience over the past six years as well as broader analysis of the scientific literature and technological developments, in many cases the ion-conducting materials and layers are the key limitation to realizing improved cell performance. Following are three specific examples:

- ARPA-E has invested in numerous battery chemistries that use lithium metal as the negative electrode material (e.g., Li/S, Li/O_2, Li/metal oxides), but while there are promising approaches under development to enable the use of lithium metal, thus far no commercially viable approach has been unambiguously demonstrated in practical cell formats and with practical operating conditions. The lack of an ion-conducting separating layer with the required attributes is the key limitation.[5]
- In cells that use solid oxide membranes for electrometallurgy (e.g., for the production of the light metals Al and Mg), the poor chemical stability of the solid oxide membrane in the high temperature molten baths is often the key limiting factor. [6]
- Numerous electrochemical cells would benefit from a stable anion-exchange membrane (AEM) with attributes similar to those of Nafion (a cation-exchange membrane), but a commercially viable layer has not yet been developed.[7-9]

Much of the challenge for achieving improved ion-conducting materials and layers stems from the need for numerous attributes to be achieved simultaneously. This RFI is specifically interested in materials and layers with ion selectivity and, as appropriate, selectivity for other species such as electrons and neutral molecules. Additional attributes that are typically of interest include high ionic and appropriate electronic conductivity (low for pure ionic conductors, high for mixed ionic/electronic conductors), chemical and thermal stability, good mechanical properties, ease of integration with other cell layers, cost-effective manufacturing, and other features required by the application. For example, for mobile electrochemical devices mass and volume are important, so the density and thickness of ion-conducting materials and layers are important. Figure 1 provides a qualitative visualization of a sample of the numerous important attributes. Figure (1)(a) shows examples of two ion-conducting materials, one an oxide conductor (δ-Bi_2O_3) and one a Li-conductor (LIPON). Each of these materials has at least one excellent attribute, but other attributes suffer serious limitations. This is often the case with ion-conducting materials or layers and ARPA-E seeks ideas on how to achieve excellence across the full set of attributes, as shown in Figure (1)(b). Note that each example in Figure (1)(a) is a particular composition, but this set of attributes could just as easily apply to a multi-component ion-conducting layer as to a particular composition. Researchers typically focus on only one or a few of the properties shown in Figure 1 (ionic conductivity is by far the most common while mechanical properties are rarely reported), which has thus far limited commercial impact.

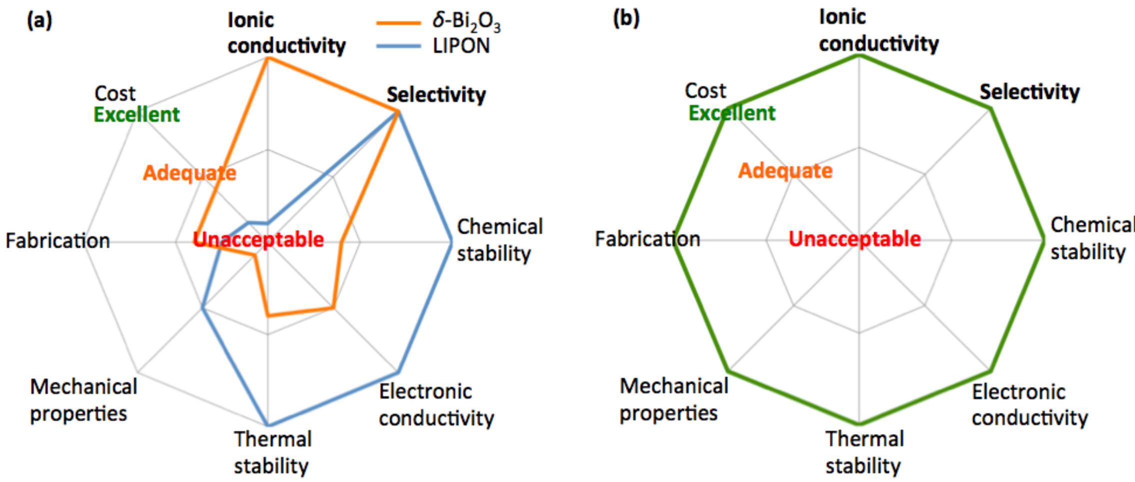

Figure 1. Radar charts showing a sample set of attributes that must be achieved simultaneously to enable a practical device. Ionic conductivity and selectivity are required attributes for this RFI, and are shown in bold. (a) shows examples of two specific materials while (b) shows what is desired. LIPON=$Li_xPO_yN_z$

ARPA-E emphasizes the need for innovations to be deeply informed by the inextricable links among materials, fabrication, and device integration. These three areas are shown as a Venn diagram in Figure 2, and these areas – and especially the regions of overlap among them – are where ARPA-E seeks innovations. Opportunities for innovation in the regions of overlap are driven in part by the frequent tradeoffs among the attributes shown in Figure 1. As a simple example, reductions in the area-specific resistance (which determines power) may be achieved either by a reduction in the thickness of a conducting layer or by developing a layer with a higher conductivity and the same thickness. These approaches have significantly different implications for required mechanical properties and fabrication methods. The following examples have been identified by ARPA-E as promising examples of innovations in each of the areas in Figure 2. While these examples are discussed separately, emphasis is again placed on the need to consider all three areas simultaneously.

- In the area of materials, new compositions of ion-conducting materials are of interest, [10] as are innovations that make use of existing ion-conducting compositions while improving the attribute set shown in Figure 1 (these may be called "non-compositional material enhancements"). Composites [11, 12] and nanostructuring [13] are two examples.
- In the area of fabrication there are now examples of very thin (20-40 micron), self supported, flexible, polycrystalline ceramic ion-conducting layers, [14] albeit with a material (3YSZ) with a fracture toughness 3-5x higher than typical ceramic conductors. Additionally, epitaxial growth has been shown to enhance chemical stability in heterostructures.[15]
- In the area of devices, there are examples of ion conductors that are formed from the reaction of cell components (e.g., the Li-ion SEI layer, as well as the LiI solid electrolyte in Li/I_2 medical device batteries) as well as active materials that are formed from the solid electrolyte during the first charge (*i.e.*, a "battery made of one material").[16] Also at the device or process level, there are examples of the use of ion-conducting layers for process intensification, for example in the combination of reaction and separation in gas to liquids processes.[17]

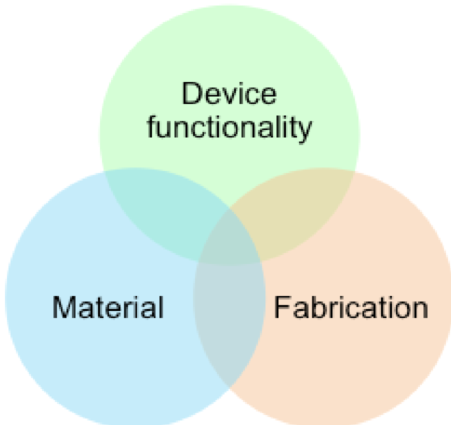

Figure 2. Venn Diagram showing the three principle areas of interest in this RFI, and their inextricable links.

While innovations that can achieve transformational improvements in a particular high-impact electrochemical cell are certainly of interest, ion-conducting materials or layers that are broadly enabling are of particular interest. Three examples of broadly enabling ion conductors include yttria-stablized zirconia (YSZ), an oxide conductor, beta"-alumina, which has been used primarily as a Na^+ conductor, and Nafion, a cation conductor (e.g., Na^+ and H^+). Each of these materials has been used in numerous electrochemical cells that either already impact, or have the potential to impact, ARPA-E's mission areas.

ARPA-E is thus seeking input from diverse research and development communities with regard to making advances in selective ion-conducting materials and layers.

Purpose and Need for Information:

The purpose of this RFI is solely to solicit input for ARPA-E consideration to inform the possible formulation of future programs intended to help create transformative selective ion conductors for electrochemical cells. Information obtained may be used by ARPA-E on a non-attribution basis. This RFI provides the broad research community with an opportunity to contribute views and opinions regarding ion conductors. Based on the input provided to this RFI and other considerations, ARPA-E may decide to issue a formal FOA for this area. If a formal FOA is issued, it will be issued under a new FOA number.

REQUEST FOR INFORMATION GUIDELINES:

Comments in response to this RFI should be submitted in PDF format to the email address ARPA-E-RFI-Ion-Conductors@hq.doe.gov by **5:00 PM Eastern Time on September 18, 2015**. ARPA-E will not review or consider comments submitted by other means. Emails should conform to the following guidelines:

- Please insert "Responses for RFI for FOA DE-FOA-0001396" in the subject line of your email, and include your name, organization, email address, and telephone number in the body of your email.
- Respondents are requested to include the following information as part of the response to this RFI:
    - Company/Institution name;
    - Individual contact name and title;

- Phone number;
- Email address;
- Type of company/institution (e.g.. university, non-governmental organization, small business, large business, federally funded research and development center (FFRDC), government-owned/government-operated (GOGO)); and
- Area of expertise.

Questions: ARPA-E encourages responses that address any subset of the following questions of relevance to the respondent and also encourages the inclusion of references to important supplementary information.

1) **In what electrochemical cells can improved ion conductors make a transformative difference? What attributes are required?**
   a) Describe electrochemical cells in which enhanced ion-conduction functionality would make a transformative difference in cell performance and ultimately process economics. ARPA-E is interested in cells where the ion conductor is the dominant challenge, and also in the applications that could be impacted by the creation of a broadly enabling ion conductor.
      i) What is the application area or areas?
      ii) What is the typical process diagram, and what are the typical electrochemical cell materials and construction?
      iii) To the extent possible, quantify the extent to which the ion conductor contributes to cost and performance metrics such as $/W, $/Wh, $/Wh-cycle, $/kg, W/L, Wh/kg, etc. In other words, if an ion conductor with "perfect" properties (e.g., as shown in Figure (1)(b)) were available, and it were free, how much would that change the overall performance and economics of the electrochemical cell? For example, in a solid oxide membrane cell used for light metal production what is the contribution of the solid oxide membrane itself to the $/kg and kWh/kg of metal produced?
   b) What are the gaps between the attributes presently available and the attributes needed to make a transformative advance for the cell or cells described in 1) a)? In other words, provide a version of Figure (1)(a) with as many quantitative attributes as possible.

2) **Technical opportunities**
   What technical opportunities could ARPA-E pursue in a potential program in selective ion-conducting materials and layers? Technical opportunities may include concepts that have not yet been explored, recent scientific advances, ideas drawn from existing technologies or practices in unrelated industries, etc.
   a) Technical opportunities in the area of materials.
      i) What are examples of new ion-conducting compositions or material classes? Both pure ionic conductors and mixed ionic and electronic conductors are of interest. Which of the attributes (such as those shown in Figure 1) have been quantified, what are the values, and how do the values compare with targets?
      ii) What are examples of material enhancements that do not depend on the creation of new conductive phases? Which of the attributes (such as those shown in Figure 1) have been quantified, what are the values, and how do the values compare with targets?
      iii) What is known about the links among key attributes such as those shown in Figure 1? In other words, what knowledge do we have on the tradeoffs among key attributes that can be

used to stimulate innovations that allow us to simultaneously maximize all attributes of interest?

b) Technical opportunities in the area of fabrication.
    i) What are examples of new ways of making ion-conducting materials that can help achieve the relevant attributes (especially mechanical properties and cost) shown in Figure 1?
    ii) Ion-conducting layers in electrochemical cells that will significantly impact ARPA-E mission areas will ultimately need to be fabricated with enormous cross-sectional areas. Are there opportunities to incorporate ion-conducting phases within a matrix that significantly advance the overall set of attributes towards that shown in Figure (1)(b)? More generally, what are innovative ideas for to create ion-conducting layers with enormous areas and low cost?
    iii) Can vapor deposition processes be applied to ion-conducting materials while still meeting targets for cost and other attributes? What deposition rates are required? Are there particular solid ion conductor material classes well suited to high-rate vapor deposition?
    iv) What fabrication processes from other industries, in addition to vapor deposition, can potentially be brought to bear on solid ion conductors?
    v) What fabrication processes can substantially reduce interfacial resistance?

c) Technical opportunities in the area of devices and processes.
    i) What ideas at the device level may allow significant gains in ion-conducting functionality, integration, cost, or other attributes?
    ii) Are there existing processes or electrochemical cells in which the use of a selective ion conductor could result in significant benefits?

d) What technical examples from unrelated industries can serve as inspiration for ion conductor development, especially in the context of the need for numerous attributes as shown in Figure 1? What industries create thin functional layers in which at least some of the attributes are the same as those shown in Figure 1?

3) Methodology, measurement, and analysis

While ARPA-E does not support pure methodology development, ARPA-E is interested in the application and customization of existing methodologies, as well as analysis that may inform the creation of quantitative material and layer targets.

a) Computations
    i) How can DFT and other methods derived from electronic structure calculations lead to experimental breakthroughs during a three-year project? What about other modeling methodologies such as molecular dynamics?
    ii) How would a well-designed, well-curated, database of all quality, publicly available solid ion conductor property values facilitate advances by computational and experimental researchers?
    iii) What property values shown in Figure 1, or others of importance for creating new solid ion conductor functionality, can be computed with sufficient accuracy to be able to contribute to development efforts?
    iv) To what extent can current computational methods predict ion conductivity at grain boundaries? Are there promising new approaches to enhance our ability to make such predictions?

b) Experiments
    i) What property values shown in Figure 1 (or others of importance) whose availability would significantly advance progress are missing from the literature at a sufficient level of accuracy?

ii) What measurements can be made early in the development cycle in order to de-risk later investments?
iii) Are there measurements that are not done routinely today that could significantly enhance understanding or knowledge and thereby accelerate development efforts?

c) Analysis
   i) What scientific and engineering analysis has been done, or needs to be done, to provide quantitative targets for attributes shown in Figure 1?

4) **Teaming**
ARPA-E seeks to identify the technical competencies and organizations with the drive and capabilities to generate transformative concepts and significantly advance them towards commercial deployment. ARPA-E encourages the creation of teams of diverse technical expertise and diverse institutional affiliation.
a) What technical disciplines can contribute to this effort? Which individual researchers and organizations could contribute to a potential program?
b) What industries working in different, but potentially related, areas could contribute to a program in ion-conducting materials and layers?

Specifically Not of Interest to this RFI:
The following items, while they may be generally related to the discussion and questions above, are not of interest for the present RFI:

- Advances in porous layers in which liquid electrolytes are present and allow the passage of ionic current through the transport mechanisms typically found in liquid electrolytes. Such layers are not of interest because they do not allow for selectivity among ions and potentially neutral species, and ion selectivity is one of the attributes of specific interest in this RFI.
- Incremental improvements in ion-conducting materials and layers that have already received significant attention from other funding agencies. For example, incremental improvements in perfluorosulfonic acid (PFSA) and polybenzimidazole (PBI) membranes for automotive fuel cells, or in high-temperature oxide conductors such as YSZ for SOFCs, are not of interest in this RFI.
- Materials that conduct ions but whose main function in a cell is something other than ionic conduction. For example, materials that intercalate ions for the primary purpose of energy storage are not of interest.
- Innovations in electrochemical cells or devices that primarily focus on functionality other than ion conduction.
- Open-ended basic research aimed at materials discovery. While such work is of great value it is not a good fit for ARPA-E support.

Additional information and guidelines:

- Responses to this RFI are limited to no more than 10 pages in length (12 point font size).
- **Responders are strongly encouraged to include preliminary results, data, and figures that describe their potential methodologies.**
- **PROPRIETARY INFORMATION:** Because information received in response to this RFI may be used to structure future programs and FOAs and/or otherwise be made available to the public, **respondents must NOT include any information in their responses that might be considered business sensitive, proprietary, or otherwise confidential.** Responses must be submitted with the understanding that their contents may be publicly disclosed and, in the event of a public

disclosure, DOE will NOT notify respondents or provide any opportunity to revise or redact submitted information. If you want to separately submit relevant proprietary or confidential information, include in your response a non-proprietary summary of the information you would like to submit. You may be contacted for a more specific description that may include proprietary or confidential information. If so, you will receive written instructions on where and how to submit such information, including any necessary markings on the submission to protect the confidential/proprietary information.

- ARPA-E will not pay for information provided under this RFI, and there is no guarantee that a project will be supported as a result of this RFI. This RFI is not a FOA, and ARPA-E is not accepting applications for financial assistance under this RFI. Responses to the RFI will not be viewed as any commitment for the respondent to develop or pursue the project or ideas discussed. ARPA-E may decide at a later date to issue a FOA based on consideration of the input received from this RFI. No material submitted for review will be returned and there will be no formal or informal debriefing concerning the review of any submitted material. ARPA-E reserves the right to contact a respondent to request clarification or other information relevant to this request. All feedback provided will be taken into consideration, but ARPA-E will not respond to individual submissions or publish publicly a compendium of responses.

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