Significant Research Outcomes[1]

U.S.-China Clean Energy Research Center (CERC) Clean Vehicle Consortium (CVC)

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1. Advanced Batteries [Thrust Area 1]

- ***Characterizing degradation mechanisms to improve battery performance:*** CERC research efforts by Argonne National Laboratory, Sandia National Laboratories, and University of Michigan (U.S.) and Tsinghua University (China) together laid the groundwork for rational strategies to limit a pervasive degradation process in lithium-ion batteries with cathodes based on manganese (Mn). These batteries offer environmental, safety, and cost advantages over other types of Li-ion batteries, yet their service life is shorter. The long-standing degradation problem is caused by Mn from the cathode dissolving into the electrolyte as the battery is charged and discharged. The dissolution process can destabilize electrolyte/electrode interfaces, reducing battery capacity and cyclability. Mn was found to exist in an ionized (+2) state, rather than as Mn metal, suggesting that a metathesis reaction is responsible for incorporation into the solid electrolyte interphase. The work has been published in *Nature Communications*[2]. Separately, researchers modeled the atomic scale processes associated with electrolyte/electrode reactions at Mn-containing cathodes, revealing that solvent decomposition on cathode surfaces becomes more facile as the battery is charged, and proceeds via a two-step process: H-abstraction followed by ring-opening. This work was reported in the *Journal of the Electrochemical Society*[3]. (CERC-CVC Phase 1)

- ***High energy density batteries****:* CERC researchers from the University of Michigan (U.S.) in collaboration with Tsinghua University and Beijing Institute of Technology (China) have been exploring "Beyond Li-ion" battery chemistries based on the sodium-oxygen couple (i.e, "sodium-air" batteries). The primary discharge product in sodium−air batteries has been reported in some experiments to be sodium peroxide (Na_2O_2), while in others, sodium superoxide (NaO_2) is observed. Importantly, cells that discharge to NaO_2 exhibit high

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[1] In addition to Significant Research Outcomes, further information about each project, including partners, research objectives, collaboration, and other details are available in the Project Fact Sheets: http://www.us-china-cerc.org/pdfs/CVC_Factsheets_Phase%201_Final.pdf

[2] Zhan, Lu, Kropf, Wu, Jansen, Sun, Xiu, and Amine (2013). "Mn(II) deposition on anodes and its effects on capacity fade in spinel lithium manganate–carbon systems". Nature Communications 4. Article Number 2437. http://www.nature.com/articles/ncomms3437

[3] Kumar, Leung, and Siegel (2014). "Crystal Surface and State of Charge Dependencies of Electrolyte Decomposition on LiMn2O4 Cathode". J. Electrochem. Soc. 2014 volume 161, issue 8, E3059-E3065. http://jes.ecsdl.org/content/161/8/E3059.abstract

efficiencies, while those that discharge to Na_2O_2 do not. To explain these differences, researchers used density functional and quasi-particle GW approximation methods to comparatively assess the conductivities of NaO_2 discharge phases by calculating the concentrations and mobilities of intrinsic charge carriers in Na_2O_2 and NaO_2. In the case of Na_2O_2, the transport properties are similar to those found in earlier CVC research for lithium peroxide, suggesting low bulk conductivity. Transport in NaO_2, has some features in common with the peroxide but also differs in important ways. Similar to Na_2O_2, NaO_2 is predicted to be a poor electrical conductor, wherein transport is limited by sluggish charge hopping between O_2 dimers. Differing from Na_2O_2, in NaO_2 this transport is mediated by a combination of electron and hole polarons. An additional distinguishing feature of NaO_2 is its ionic conductivity, which is 10 orders of magnitude larger than the electronic component. The ionic component is comprised primarily of p-type contributions from (surprisingly mobile) oxygen dimer vacancies, and from n-type contributions from negative sodium vacancies. In the context of sodium−air batteries, the low electronic conductivity afforded by NaO_2 suggests that enhanced bulk transport within this phase is unlikely to account for the higher efficiency exhibited by this system. Rather, the enhanced efficiency of NaO_2-based cells should be attributed to other factors, such as a reduced tendency for electrolyte decomposition. This work was reported in *Chemistry of Materials*[4]. (CERC-CVC Phase 1)

- ***In-situ measurement of lithium transport in electrodes****:* CERC researchers from the Ohio State University (U.S.) in collaboration with Tsinghua University (China) have developed a non-destructive method to quantify lithium (Li) transport in a Li-ion cell in real time. By enabling exceptional sensitivity in the temporal and spatial measurement of Li transport, this technique can help to guide materials development to improve the efficiency of energy storage mechanisms. The method, which is based on *in situ* neutron-depth profiling (NDP), has been used to measure the Li distribution upon charge and discharge in a high-capacity silicon anode. The onset of lithiation was visualized, revealing the enrichment of Li atoms on the anode surface followed by their propagation into the bulk. Similarly, the delithiation process showed the removal of Li near the surface, resulting in decreased coulombic efficiency, likely because of trapped Li within the intermetallic material. This work was reported in *Angewandte Chemie*[5] and made the cover of that issue of the journal. (CERC-CVC Phase 1)

- ***Development of high energy battery system with 300wh/kg:*** CERC research team in Argonne National Laboratory (U.S.)and Beijing Institute of Technology (China) are working together to explore the structural degradation and low conductivity of transition metal

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[4] Yang and Siegel (2015)."Intrinsic Conductivity in Sodium–Air Battery Discharge Phases: Sodium Superoxide vs Sodium Peroxide". *Chem. Mater.*, **2015**, *27* (11), pp 3852–3860. http://pubs.acs.org/doi/abs/10.1021/acs.chemmater.5b00285

[5] Liu, Wang, Pan, Qiu, Canova, Cao, and Co (2014). "In Situ Quantification and Visualization of Lithium Transport with Neutrons". Angewandte Chemie Vol. 53, no. 36: 9498 - 9502. http://onlinelibrary.wiley.com/doi/10.1002/anie.201404197/abstract

oxides that leads to severe capacity fading in lithium-ion batteries.
The team designed specific hierarchical structures and demonstrated their use in flexible, large-area anode assemblies. Fabrication of these anodes is achieved via oxidative growth of copper-oxide nanowires onto copper substrates followed by radio-frequency sputtering of carbon-nitride films, forming freestanding three-dimensional arrays with core–shell nano-architecture. Cable-like copper oxide/carbon-nitride core–shell nanostructures accommodate the volume change during lithiation−delithiation processes; the three-dimensional arrays provide abundant electroactive zones and electron/ion transport paths; and the monolithic sandwich-type configuration without additional binders or conductive agents improves energy/power densities of the whole electrode. The work was published in *Nature Communications*.[6] (CERC-CVC Phase 2)[7]

2. Vehicle Technologies [Thrust Area 2]

- ***Novel materials facilitate conversion of waste heat to electricity:*** CERC scientists from the University of Michigan (U.S) and the Wuhan University of Technology (China) jointly developed a novel approach for fabricating bulk thermoelectric materials. Based on the self-propagating high temperature combustion synthesis (SHS), this controlled combustion process uses the heat of an exothermic reaction to rapidly and spontaneously fuse elemental powders into the desired compound. The SHS process had been believed to require temperatures above 1800 K, but the CERC research team shows that it can be used to synthesize at even lower melting-points. The team developed a new criterion for the applicability of SHS to all materials, including high-temperature refractories. The work was published in *Nature.*[8] This research opens a new avenue for the ultra-fast, low-cost, large-scale production of thermoelectric materials and provides new insights into combustion. The SHS process is being applied to a variety of thermoelectric materials. Most recently, the research team developed an ultra-fast, one-step fabrication process for legs of thermoelectric modules that are provided with Ni-Al electrodes for rapid assembly. This process utilizes plasma activated reactive sintering technique. (CERC-CVC Phase 1)

- ***Power-weighted efficiency analysis for rapid sizing****:* CERC researchers from University of Michigan (U.S.), Tsinghua University and Shanghai Jiao Tong University (China), are developing techniques to model, analyze, design, and control power-split hybrid powertrains—enabling their use in heavier vehicles that require multiple planetary gears and multi-mode operation. The research team's design methodology is about 12,000 times faster

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[6] Tan, Wu, Yuan, Chen, Zhao, Yao, Qian, Liu, Ye, Shahbazian-Yassar, Lu and Amine (2016). "Free-standing three-dimensional core-shell nanoarrays for lithium ion battery anodes". Nature Communications 7, 11774, 2016. http://www.nature.com/articles/ncomms11774

[7] Research in progress. The paragraph highlights the preliminary outcomes.

[8] Zhao, Lo, Zhang, Sun, Tan, Uher, Wolverton, Dravid and Kanatzidis (2014). "Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals". Nature 508, 373-377, 2014. http://www.nature.com/nature/journal/v508/n7496/abs/nature13184.html

than dynamic programming and similar optimization methods. This project was selected as one of the "pathways to implementation" projects. (CERC-CVC Phase 1)

- ***Computationally efficient algorithms for steady-state simulation of electric machines:*** CERC researchers at the University of Michigan (U.S.) in collaboration with Tsinghua University (China) developed new algorithms to aid in the analysis and design of electric machines. These algorithms efficiently calculate an electric machine's torque and power losses under steady-state operating conditions. The models capture frequency-dependent phenomena needed to accurately calculate the power lost in conducting regions of the machines, such as permanent magnets and windings. A MATLAB toolbox, made available to all CERC members, provides a stand-alone, electric machine modeling and simulation environment. A project, sponsored by CERC industrial partner DENSO, used this toolbox in the design of a high-performance in-wheel electric motor for battery electric vehicles. Algorithms in this new methodology can be over 100 times faster at estimating steady-state losses than algorithms used in some commercial software, potentially accelerating the design of electric machines used in hybrid or electric vehicles. (CERC-CVC Phase 1)

- ***Functional safety and torque security of electrified powertrains***: CERC researchers from the Ohio State University (U.S.) and Beijing Institute of Technology, Shanghai Jiao-Tong University, and Hefei University of Technology (China) developed a methodology for model-based design of diagnosis and fault-tolerant control of electrified powertrain that is consistent with the ISO 26262 standard on automotive functional safety. The methodology has been applied to the problem of ensuring torque security (that is, preventing unintended acceleration) in electric and hybrid-electric vehicles. This project was selected as one of the "pathways to implementation" projects. (CERC-CVC Phase 1)

- ***Joining in multi-material structures****:* CERC researchers at the University of Michigan (U.S.) and Shanghai Jiao Tong University (China) developed a hybrid, electrically assisted, friction stir welding (FSW) process for joining dissimilar materials. The objective is to reduce mechanical welding force during the traditional FSW process and enhance the joint quality of aluminum welded to steel. The research team developed a hybrid FSW system that introduces a high-density electrical current around the tool during welding. The electro-plastic effect and resistance heating help soften the material, reduce the welding force, and enhance the stirring action on the two materials. Researchers studied the effects of different process parameters and observed micro-interlock features and an intermetallic compound layer of 1 micron thickness at the Al-Fe interface (on the joint cross sections perpendicular to weldline). The highest tensile strength can reach 85% of the base aluminum alloy. The team also developed two multiple-phase flow models, one for the transient plunge stage, and one for the stable welding stage, to help improve understanding and optimize FSW of dissimilar materials. (CERC-CVC Phase 1)

- ***Modeling the strength of hybrid-material interfaces:*** Researchers at the University of Michigan (U.S.), in collaboration with Eaton Corporation (U.S.), developed techniques to measure the properties of adhesives used in the bonding of hybrid materials. Classical fracture mechanic approaches do not work on these materials because well-made joints lack well-defined cracks and the extent of mode mixing in hybrid joints cannot be determined *a priori*. The researchers used digital-image correlation for use in cohesive-zone models and showed how cohesive properties (mode-I and mode-II traction-separation laws) can be obtained for an adhesively bonded interface. These cohesive properties were incorporated into finite-element analyses of a hybrid-material gear system to evaluate the approach as a design tool for lightweight structures in the automotive industry. (CERC-CVC Phase 1)

3. Connected and Automated Vehicles [Thrust Area 3]

- ***Electric vehicle (EV) charging station simulations****:* Researchers from the Ohio State University (U.S.) and Tsinghua University (China) completed simulations of EV charging station strategies to optimize coordination of the electricity and transport systems. Researchers found that high penetration of EVs can significantly stress the distribution-level infrastructure, including accelerated aging of distribution transformers. Their work demonstrates the benefit of using charging control strategies to mitigate these effects and to potentially reduce the cost of charging energy. (CERC-CVC Phase 1)

- ***Control strategies for vehicle-grid integration****:* Strategies to minimize grid impacts from the large-scale charging of plug-in electric vehicles (PEVs) tend to focus on exploiting the overnight valley in electricity demand. However, such strategies raise the possibility of overloads in the local distribution system and accelerated battery degradation. Researchers at the University of Michigan (U.S.) and Beijing Institute of Technology (China) established a PEV charging framework that balances total generation costs with local costs caused by overloads and battery degradation. Solving the resulting large-scale optimization problem involves each PEV minimizing its charging cost with respect to a forecast price profile while taking into account local grid and battery effects. Charging strategies proposed by participating PEVs are used to update the price profile, which is subsequently rebroadcast to the PEVs. The process then repeats. Under mild conditions, this iterative process converges to yield a unique, efficient (socially optimal) coordination strategy. (CERC-CVC Phase 1)

- ***Wireless charging of electric vehicles with extremely high efficiency****:* Researchers from University of Michigan-Dearborn and University of Michigan-Ann Arbor (U.S.) and Northwestern Polytechnical University and Chongqing University (China) developed a high-efficiency method to wirelessly charge electric vehicles. This power-transfer method uses a double-sided LCC circuit to provide far better efficiency and controllability than existing topologies, automatically tuning the resonance, so that neither the efficiency nor the amount of power transfer degrades excessively with increased distance or misalignment. This approach greatly improves overall efficiency, with DC-to-battery efficiency exceeding 96% at 8 kW output power. The team also developed a capacitive wireless transfer system especially suited for dynamic roadway EV charging. This new system adapts the LCLC structure to provide high efficiency (up to 92%), increased tolerance for misalignment, and stable and consistent power transfer (prototype rated up to 3.3 kW). (CERC-CVC Phase 1)

4. Systems Assessment [Thrust Area 4]

- ***Life-cycle analysis and energy and environmental impacts of technology**:* CERC researchers from Argonne National Laboratory, University of Michigan, and Aramco Service (U.S.) are collaborating with researchers from China Automotive Technology & Research Center and Tsinghua University (China) to develop modeling capabilities for life-cycle analysis (LCA) and impact assessments of clean vehicle technology deployment based on the current modeling platform or approach for both the U.S. and China. Building on the success of two open source worldwide-used models, GREET (LCA model) and VISION (fleet impact model) developed by Argonne National Laboratory, the team is now developing the Chinese version of GREET and VISION models. These modeling capabilities allow the researchers to conduct LCA and impact analyses on specific clean vehicular technologies to assess energy and environmental impacts under different market penetration scenarios in both U.S. and China. (CERC-CVC Phase 2)[9]

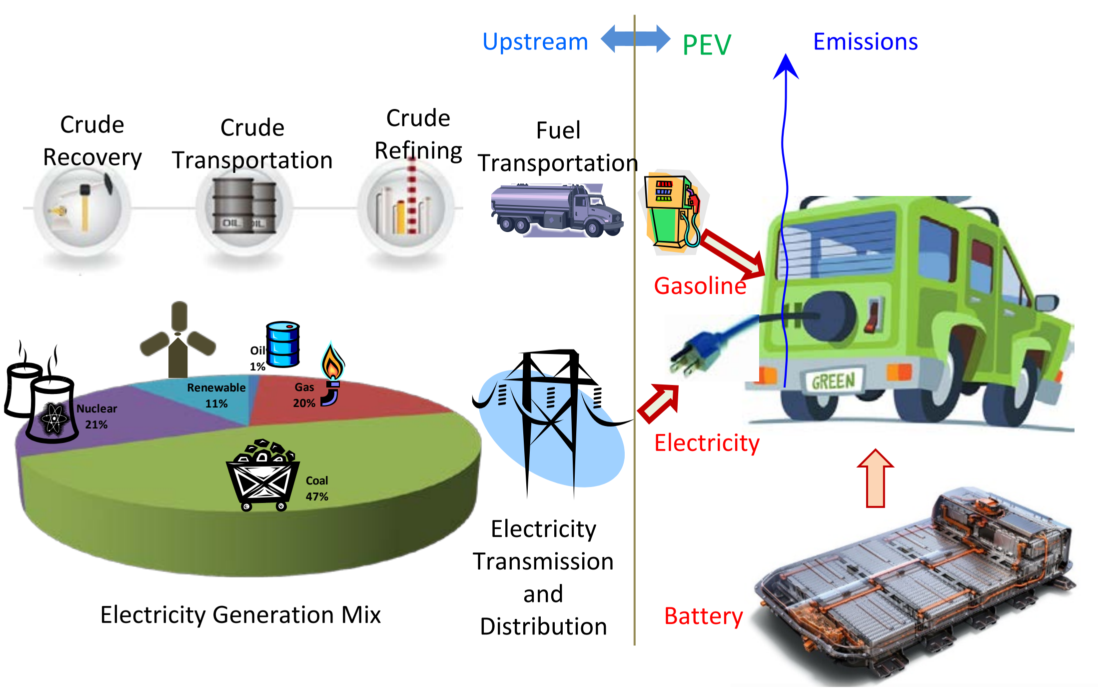

Figure 1: Life-cycle analysis of Electric Vehicles and Batteries

[9] Research in progress. The paragraph highlights the preliminary outcomes.

- ***Life cycle assessment of wirelessly charging electric vehicles****:* CERC researchers from University of Michigan-Ann Arbor, University of Michigan-Dearborn, DENSO, Delphi, Oak Ridge National Laboratory (U.S.) collaborated with Beihang University) and KAIST (Korea) to assess the life cycle benefits of a wireless-charging technology for an urban electric bus system. The team's integrated life-cycle assessment and cost model found that the more frequent charging typical of wireless technology would enable a bus system to significantly downsize and lower the cost of its on-board batteries, helping to offset wireless infrastructure costs. The downsized battery also lightweights the buses to improve fuel economy. The team conducted a detailed inventory of charging hardware and a case study of the Ann Arbor bus system. It found that a wirelessly charged electric bus system is comparable to a plug-in charging electric bus system in terms of its energy consumption, greenhouse gas emissions, and costs on a life-cycle basis. Current research is assessing the wireless charging of passenger cars to determine the potential for this technology to enhance the sustainability of urban transportation. (CERC-CVC Phase 1 and Phase 2)

- ***Improving precision of electricity grid modeling to assess EV sustainability***: Air pollutant emissions from electricity generation vary spatially and temporally. Accurate modeling of greenhouse gases and other emissions from EV charging and electricity-intensive industries is critical to assess the environmental performance of clean vehicle technologies. CERC researchers developed a new emissions model that better accounts for the imports and exports of electricity associated with a defined grid. The research team's "nested average electricity allocation model" indicates that emissions are dramatically higher than those reported. For example, the model demonstrated that in the aluminum (Al) industry, the U.S. production-weighted average emission factors was 19.0 and 19.9 kilograms of CO_2-equivalent per kg of primary Al ingot produced. Previous studies reported it as 10.5 and 11.0 kilograms of CO_2-equivalent per kg of primary Al ingot produced. (CERC-CVC Phase 1)