



# **Innovations in Army Energy and Power Materials Technologies**

Edited by

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# Preface

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This compendium captures the considerable experience and technical depth residing within the US Army Research Labratory (ARL) specifically within the area of Energy and Power (E&P) technologies. ARLEnergy and Power Division researchers leverage an extensive partner network within the lab, with academe, with the Army Research Development and Engineering Centers, with other services and agencies, and with industry.

#### **Defense Science and Technology Context**

The primary purpose of this work is to document the "why, what and how" of Army research in the E&P area, providing a snapshot of how top-driven Army needs and bottom-up internal discovery and innovation are reconciled in practice by investigator approaches and results. As such, we hope to convey not only why we are researching selected aspects of energy and power areas, but the unique aspects and dynamics of the Army/ defense research milieu that distinguish the work from strictly academic inquiry or commercial product focused efforts.

ARL is part of both the Department of Defense (DoD) as well as the Army Research and Engineering (R&E) enterprise. We work closely in partnership with other labs and activities within this enterprise. DoD's research and engineering focus, led by the Assistant Secretary of Defense for R&E within that enterprise, is critical to the nation's defense. DoD R&E strategic guiding imperatives include:

- 1. Mitigate current and emerging adversary threats that could degrade U.S. (and allied) capabilities;
- 2. Affordably enable new or extended capabilities in existing military systems;
- 3. Create technology surprise through science and engineering applications to military problems.

These imperatives complement the seven DoD S&T priority areas which provide the focus to meet future technological goals. Three of these areas address "Complex Threats" (Electronic Warfare/ Electronic Protection; Cyber Science and Technology; and

Counter Weapons of Mass Destruction); the remaining four enable "Force Multipliers" (Data-to-Decisions; Autonomy; Engineered Resilient Systems; and Human Systems). DoD/joint and service S&T portfolios are organized to address these priorities and are augmented by ten significant underpinning technology areas, each of which has a "Community of Interest" (COI) to advise DoD and service S&T leadership on the health of US defense focused efforts in these areas [1]:

- Advanced Electronics
- Air Platforms Biomedical
- Counter-Improvised Explosive Devices
- Energy & Power Technologies
- Ground & Sea Platforms
- Materials and Manufacturing Processes
- Sensors & Processing
- Space
- Weapons

The technologies addressed within this compendium most closely align to the Energy & Power COI, focused on E&P technologies to enable and enhance operational capabilities and effectiveness.

Both DoD and the Army use a "Technologies Taxonomy" to help organize, coordinate, and analyze S&T efforts in underlying areas across activities as well as to help inform interagency (e.g. Department of Energy, National Aeronautics and Space Administration) S&T engagements. For example, DoD and Army E&P taxonomy includes the following areas:

• Electromechanical Conversion: Increase the power density, efficiency, and robustness of motors, generators, and actuators while also reducing their life cycle costs.

• Energy Storage: Improve electrical and electrochemical energy storage devices to decrease device size, weight, and cost as well as increase their capabilities in extreme temperatures and operating conditions.

• **Power Control and Distribution**: Develop tactical, deployable power systems using conventional fuels, alternative fuels, and energy harvested from renewable/ambient sources.

• **Power Generation/Energy Conversion:** Enable smart energy networks for platforms, forward operating bases, and facilities using modeling and simulation tools as well as new, greater capability and efficiency components.

• **Thermal Transport and Control:** Efficiently manage heat and enable higher power density systems through advanced thermal science and technology: advanced components, system modeling, and adaptive or hybrid-cycle technologies.

#### **Defense and Army Laboratories Context**

DoD laboratories execute mission areas within the DoD Research and Engineering Enterprise as outlined above. These mission areas continue to evolve to address both common DoD as well as service specific needs and priorities. Traditionally, DoD labs, including ARL, have been responsible for conducting basic science, supporting technology transition, and facilitating acquisition of technology for DoD/Army (smart buyer):

"The Labs' traditional missions are defined as "high quality science, technology transition, and smart acquisition." While these missions remain important and relevant, the rapidly changing technology and threat landscapes dictate the Labs should also adapt their missions to continue serving the warfighter; this includes an expanded set of missions to focus on technology leadership, open innovation, and technology defense." [2]

The Defense Science Board Task Force Report [2] notes that DoD labs should embrace open innovation by engagement with non-traditional defense R&T partners, and incorporate: Technology Leadership (supporting DoD through disruptive and emerging major technology shifts); Technology Defense (protecting US technological advantage); and Open Innovation (better tapping and integrating technologies developed outside of DoD).

ARL has several initiatives that are enabling such an open innovation environment: ARL Open Campus and ARL Extended. Open Campus is providing more seamless mechanisms and access for partners to work with ARL researchers while ARL Extended is establishing ARL research innovation hubs in selected geographic areas within the United States. As an early adopter of Open Campus, the ARL Energy & Power Division established the Center for Research in Extreme Batteries (CREB). CREB leverages resources from ARL and funding from industry, academic, and Government partners, to initiate collaborative projects. The consortium is sponsoring novel battery research with a focus on extreme performance parameters and environments. A CREB technical accomplishment (detailed in this compendium) is a recent discovery of "water in salt" aqueous electrolytes which offers potential new directions for energy storage and water science.

#### ARL Technical Strategy

As the Army's corporate research lab, ARL conducts relevant, transformative research rooted in the tenets of discovery, innovation, and transition to deliver S&T options to meet the complex demands of the future multi-domain battlefield. ARL recently focused its investment strategy to address Chief of Staff of the Army (CSA) priorities and shape how the future Army will fight and win in a complex world. ARL has organized its technical strategy via **S&T Campaigns** which include **Essential Research Areas** (**ERAs**) that are critical to reducing technology uncertainty, filling knowledge gaps, and identifying technology risk associated with delivering new capabilities.

**ARL's S&T Campaigns** – "a systematic course of aggressive science and technology activities envisioned to lead to enhanced land power capabilities in the deep future" - form ARL's intellectual framework for planning technical strategy, aligning and synchronizing resources, people, and infrastructure. The ARL S&T Campaigns are:

- Human Sciences
- Information Sciences
- Sciences for Maneuver
- Sciences for Lethality and Protection
- Materials Research
- Computational Sciences
- Assessment and Analysis
- Extramural Basic Research.

ARL's **Essential Research Areas** are cross-cutting, capability driven focus areas; these ERAs address both enduring and future Army challenges as well as Chief of Staff of the Army (CSA) priorities:

- Human Agent Teaming
- Artificial Intelligence and Machine Learning
- Accelerated Learning for a Ready and Responsive Force
- Cyber and Electromagnetic Technologies for Complex Environments
- Distributed and Cooperative Engagement in Contested Environments
- Manipulating Physics of Failure for Robust Performance of Materials
- Tactical Unit Energy Independence
- Science of Manufacturing at the Point of Need
- Discovery

Each S&T Campaign has key campaign initiatives (KCIs) that specifically address one or more of the ERAs. Several focus on humans collaborating closely with artificially intelligent systems on the future battlefield: *Human-Agent Teaming, Artificial* 

Intelligence and Machine Learning, and Accelerated Learning for a Ready and Responsive Force, which address, respectively, enabling highly effective information exchange between Soldiers and intelligent systems in performing warfighting functions as a cohesive team; increasing the intelligence of engineered systems to become the true teammates of Soldiers; and preparing humans to engage with intelligent systems within their team to create an effective fighting force.

The complexity of the virtual domain and its melding with the physical realm for capabilities shapes the following three ERAs: Cyber and Electromagnetic Technologies for Complex Environments, Distributed and Cooperative Engagement in Contested Environments, and Manipulating Physics of Failure for Robust Performance of Materials. The reliance of intelligent systems on wireless communication and networked processes makes them vulnerable to cyber, physical, and electronic attacks. Specific application are needed to enable dispersed entities to deliver overwhelming kinetic and non-kinetic effects while combining scalable speed, radical maneuverability, and extremely efficient payload kill mechanisms. Enabling such systems requires integrating machine intelligence and human-agent teaming concepts. Enhancing the protection properties of friendly assets, as well as the lethality of munitions requires advanced materials that can sense their environment and change their state as a consequence.

Combining foundational advances in the above mentioned ERAs with innovative ways to enhance energy independence and agility and unburden tactical units is addressed by two ERAs: *Tactical Unit Energy Independence and Science of Manufacturing at the Point of Need*. Energy independence is essential to maintaining forces in the field without resupply and the reliance on intelligent systems creates increased energy demand, and an acute need to ensure sufficient reserves of power.

The *Discovery* ERA is focused on identifying, creating, developing, and exploiting innovative yet Army-relevant fundamental science and engineering advances. Discovery is essential to ARL's mission. It helps to ensure the Army's continuing and future technological superiority, and creates future offset against our adversaries while avoiding technological surprise.

#### Energy and Power S&T Alignment

Concepts for future military operations suggest a move away from large, enduring, fixed (in time and space) forward deployed bases. As such, the need for more agile, flexible, smaller footprint, rapidly reconfigurable E&P capabilities will continue to grow. Current and planned military power and energy hardware provide limited solutions for the rapidly changing dynamics anticipated on the future battlefield. Current Army operating concepts envision units capable of cross-domain maneuver. Independent expeditionary

brigades and smaller units will need to be able to fight in a multi-domain environment. Evolving leadership, tactics, techniques, procedures, as well as underlying maneuver, support, fires, and Command, Control, Communications and Intelligence (C3I) must be technically informed. Technologies must constructively support and not overwhelm unit leaders juggling demands in the land, air, maritime, cyber and space domains while maneuvering.

ARL E&P S&T efforts are addressing these dynamic future Army needs within ARL's S&T Campaigns and ERAs. Materials, device and component work are addressed primarily via the *Materials Research Campaign* whereas more much of the integrative, more mature efforts are included within the *Sciences for Maneuver Campaign*. ARL's materials research aims to address emerging requirements and capabilities for all Army platforms, with emphasis on Photonics, Electronics, E&P, Biological and Bio-inspired Materials, Structural Materials, High Strain and Ballistic Materials, and Manufacturing Science. ARL's research in Sciences-for-Maneuver focuses on gaining a greater fundamental understanding of advanced mobility technologies that enable innovative configurations and subsystems architectures – critical to the future Army's movement, sustainment, and maneuverability.

ARL E&P power work in the **Materials Research Campaign** includes materials and devices for more compact, high density, high efficiency Energy Storage; Power Generation and Energy Harvesting; Fuel Cells and Fuel Processing; and Thermal Science solutions for Soldiers, platforms, and systems. ARL's E&P focus in the **Sciences for Maneuver Campaign** is focused on leveraging and integrating underlying materials and components for applications supporting Army mobility and advanced maneuver. Knowledge gained through these research efforts will lead to technologies for the design, fabrication, integration, control, and platforms support that will significantly improve Power Projection Superiority for the Army of 2030. Sciences for Maneuver Campaign E&P efforts encompass Energy and Propulsion; Energy Storage for Mobility; Power/Energy Conversion; Compact Power Generation; and Intelligent Power. E&P efforts within the Sciences for Maneuver Campaign continue to be refined to support Army future platform modernization.

### ESSENTIAL RESEARCH AREA: TACTICAL UNIT ENERGY INDEPENDENCE (TUEI)

ARL's ERAs are designed to ensure that researchers are addressing Army user-inspired problems in order to distinguish our work from purely academic efforts. The thinking underlying the TUEI ERA is illustrative. In future peer-contested multi-domain battlefields, Army units will be required to operate at high operational tempos in

decentralized, dispersed and semi-independent formations. Reducing overall power consumption and logistics demands will be a key enabler to realize highly mobile extended operating range and duration for extended operations. More efficient, energy dense and energy adaptable systems with increased ability to operate in degraded conditions, enhanced by more autonomous energy management will be essential in this environment.

Increases in Soldier, platform and system energy demand for capabilities have not been matched by innovations in the ability to generate power, convert and store energy, and manage and distribute power. The battlefield of the future will become increasingly digital and network-centric, with new generations of sensing, weaponry, targeting, fire control, communications, and even unmanned air and ground systems adding to the energy demand of tactical units. Additionally, emerging Army robotic and autonomous systems (RAS) will enable human-machine collaboration across all mission areas by extending the area and time over which a force can be effective. RAS capabilities are envisioned to lighten Soldier load and manually and cognitively unburden the Soldier, including for E&P.

Emerging TUEI ERA initiatives include using robotic platforms to deliver and manage small unit energy. For example, Squad Maneuver Equipment Transport (SMET) [4] platforms in development include plans to carry 1000 pounds to lighten the Soldier load, have a range of 96 km while carrying additional energy sources without resupply for up to 72 hours, be able to off-load 3 kW of electrical power, and be capable of recharging all rechargeable batteries in a dismounted Army infantry platoon.

Artificial Intelligence (AI)/ Machine Learning (ML) technology is a key enabler for future intelligent energy systems. A long term goal would be to develop autonomous self-sustaining energy capabilities enabled by AI, autonomous agents and systems, and seamless energy transfer among Soldiers, weapons systems, vehicles, and robotic platforms. This could include a hub, which could reside on a future highly mobile and agile autonomous squad support platform. Today and in the near future, energy management is done at the local and individual Soldier level. Current methods are inflexible in relation to their capability for power distribution as they have no global understanding of the overall available energy sources, no energy balance across the systems and no efficient method to impact that balance.

The TUEI ERA is also leveraging a number of ongoing research efforts to improve and realize a self-sustaining energy balance by: enabling self-sustaining autonomous systems; increasing flexibility in collecting and using locally available fuel/energy sources through development of thermophotovolatics and multi-fuel tolerant

hydrocarbon based engines; increasing the energy density of Soldier wearable and conformable batteries; augmenting Soldier and platform energy via alternative and energy scavenged power sources; mitigating high power drain components (such as Soldier radios, sensors, and computing) via low-power electronics; and enhancing mobile energy operations and flexible distribution via near- and far-range wireless power transfer.

ARL anticipates innovations that will someday enable a tactical unit to collect, store, convert and distribute as much energy as needed for tactical missions a "net-zero" unit, capable of creating as much energy as it consumes, operating within an AI/ML enabled seamless energy "cloud". Whether missions last three days, seven days, or indefinitely, the Army will be better equipped to deploy an expeditionary mobile force, under extreme, remote and perhaps unforeseeable conditions.

#### **ORGANIZATION OF THE COMPENDIUM;**

This compendium is organized to address specific technical work associated with three technical branches within ARL's Energy and Power Division: *Electrochemistry; Power Sciences; and Power Integration*. Work in the Electrochemistry Branch, currently led by Dr. Cynthia Lundgren, is focused primary within the Energy Storage and Power Generation/Energy Conversion (Novel Energy) technical areas as reflected within the E&P S&T taxonomy areas outlined previously. Within ARL, this work is primary material and component focused, including electrochemical energy storage (batteries and capacitors) and electrochemical energy conversion (fuel cells, photoelectrochemistry, and photochemistry) as presented in this compendium.

Recent Power Sciences (also known as Power Components) Branch work (up to the present) has been led by Dr. Paul Barnes. Technology focus falls primarily under the Power Generation/ Energy Conversion and Thermal Transport and Control taxonomy areas previously presented. Within ARL, power generation / energy conversion work is mostly fundamental research focused on developing compact and alternative sources of power and energy capture/recovery for Soldiers and platforms, including thermophotovoltaics; thermoelectrics; pyroelectrics; flexible photovoltaics; micropower and flexible power components; compact combustion/catalysis for compact, fuel flexible sources; and isotopic and isomeric energy sources. Thermal transport and control efforts include single and multiphase cooling materials and components, multichannel and novel power electronics cooling structures, and thermal packaging.

The research and engineering work within the Power Integration (also known as Power Conditioning) Branch is led by Mr. Bruce Geil and falls mostly under the Power Control and Distribution taxonomy area. It is arranged into three primary interactional areas.

These are: wide bandgap devices (modeling, characterization and analysis for high power/ pulse power applications); power conditioning and thermal management (designs for active (power electronics) and passive (packaging) for high power, pulse power, and military unique applications); and Intelligent energy/ energy networks (architectures, designs, and test beds for advanced control of integrated and distributed energy systems.

The research performed within Power Integration is more applied in nature compared to the work in the other two branches. The focus includes understanding power device, component, and subsystem performance to address specific needs, including Army advanced mobility/propulsion, protection, lethality, and sustainment. This research is documented in ARL technical reports as well as published reports shared primarily within the engineering community.

Prefaces to each section highlight key aspects of the work within Energy and Power Division at ARL.

[1] DoD Research and Engineering Enterprise, May 2014

(https://www.acq.osd.mil/chieftechnologist/publications/docs/ASD(R&E)\_Strategic\_Gui dance\_May\_2014.pdf)

[2] Defense Science Board Task Force "Defense Research Enterprise Assessment Report", Jan 2017

(https://www.acq.osd.mil/dsb/reports/2010s/Defense\_Research\_Enterprise\_Assessment. pdf)

[3] "Army Research Laboratory S&T Campaign Plans 2015-2035", Sept 2014

[4] Army seeks to lighten Soldier loads using robots, Army News Service, Mar 2016 (https://www.army.mil/article/163385/Army\_seeks\_to\_lighten\_Soldier\_loads\_using\_rob ots/)

# Section I

# Electrochemistry

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#### 1. Introduction

The research being conducted in the Electrochemistry Branch is arranged into 2 main areas:

Electrochemical Energy Storage: Batteries and Capacitors

Electrochemical Energy Conversion: Fuel cells, Photoelectrochemistry, Photochemistry

Much of the research performed in the Electrochemistry Branch is materials based, with efforts targeted to specific Army applications. The Army has a real and continuing need for electrochemical energy storage at all scales. Batteries and capacitors are in a wide variety of currently fielded systems such as sensors, radios, night vision goggles, weapon sights, and vehicles, and are being considered for load leveling at forward operating bases (FOB's). Fuel cells have been developed for many of the same Army applications and are currently being fielded for vehicles, unmanned aerial vehicles and squad-level battery chargers with development targeting Soldier applications. Research related to photochemistry and photoelectrochemistry are looking toward an Army future where a significantly reduced logistical footprint extends the fighting efficiency of Soldiers. The intent of this high risk / high-payoff research is to provide a basis for new approaches to warfighting. The research being conducted results in referred publications, technical reports, and briefings shared broadly within both the scientific and larger DoD community as well as patents for licensing. An introductory overview is given.

### 2. Overview

### 2.1 Electrochemical Energy Storage

This research has traditionally been focused on primary and secondary batteries for Soldier applications with the main goal being reduction in weight of the carried battery. This has

meant development of lithium (Li) metal primary and lithium-ion rechargeable batteries, which have the highest specific energy due to the light weight and standard electrode potential of Li, with the result that the bulk of the current Army battery inventory is lithium based. The goals have broadened recently to include performance related to safety, calendar life, and amortized cost. This has been the direct result of the larger range of applications that are considering electrochemical energy storage including high power applications from directed energy to battery SWaP, silent watch, and bulk storage for load leveling at FOB's.

#### 2.1.1 Primary Batteries

The Li-sulfur dioxide (Li-SO<sub>2</sub>) and Li-manganese dioxide (Li-MnO<sub>2</sub>) primary batteries have been part of the Army inventory for several decades. Efforts to improve on the specific energy of primary batteries has focused on new chemistries including Li-carbon monofluoride (Li-CF<sub>x</sub>) and Li-air. These chemistries can provide some of the highest specific energies available but also have some of the largest challenges to development for Soldier applications. Li-CF<sub>x</sub> batteries, under typical Soldier radio use conditions, generate significant heat from the discharge reaction that can result in unsafe conditions. So far, most attempts to resolve this problem have not been successful. The Li-CF<sub>x</sub> chemistry has been hybridized with Li-MnO<sub>2</sub> to address this heat issue with the resulting BA-5790 battery performing at twice the specific energy of the older Li-SO<sub>2</sub> battery. Li-air batteries require the use of a membrane system that is difficult and expensive to manufacture, susceptible to degradation during storage, and that limits cell discharge rate. The chemistry has been demonstrated in prototype cells, but further development is required before it can become commercialized.

#### 2.1.2 Lithium-Metal Rechargeable Batteries

A number of rechargeable lithium metal batteries have been investigated for their higher specific energy including Li-sulfur (Li-S), Li-MnO<sub>2</sub>, and Li-iron disulfide (Li-FeS<sub>2</sub>). The MnO<sub>2</sub> and FeS<sub>2</sub> chemistries are not fully rechargeable due to phase changes that occur in the crystal structure on discharge. Modifications to the structure using dopants and the formation of composite cathodes have not been successful enough to make these systems viable. The most promising chemistry is Li-S due to its low cost and high specific energy. The Li-S chemistry has several well-known issues that stem from the fact that the discharge products of sulfur are soluble in the electrolyte. This leads to self-discharge being a significant problem, and to the eventual passivation of the Li anode upon extended cycling. Efforts to solve this issue have been undertaken by us and others including modification of the electrolyte to reduce solubility, electrolyte additives to prevent passivation, cell design including permeable and non-permeable membranes to mitigate the solubility issue, and the reaction of sulfur with carbon or infiltration into porous carbon to immobilize it, but to date,

no commercial cells are available for use. Li metal batteries also suffer from the problem of poor Li plating that leads to safety concerns after 10s-100s of cycles. Current efforts to resolve this issue have focused on additives and conducting membranes to prevent the growth of dendrites.

#### 2.1.3 Lithium-Ion Rechargeable Batteries

Li-ion battery research has focused on three main areas, development of new electrode materials, development of new electrolytes, and development of a fundamental understanding of the interface reactions and solvation behavior that controls passivation and performance. Current electrode material development has focused on replacing the conventional 4V cathodes with a 5V systems such as  $LiNi_{0.5}Mn_{1.5}O_4$ , in order to increase specific energy. Our in-house efforts have focused on the development of lithium cobalt phosphate (LiCoPO<sub>4</sub>) (4.8V), which has 30% higher specific energy than Li-iron phosphate (LiFePO<sub>4</sub>), and improved safety over Li-cobalt oxide (LiCoO<sub>2</sub>). Progress has been steady and the scale-up to pilot scale production is underway. This work also requires the development of new electrolytes that can withstand the high voltage without oxidation and has led to the discovery of new materials such as tris(hexafluoro-iso-propyl)phosphate (HFiP) as well as the development of fluorinated electrolytes that show better oxidative stability.

The development of a better understanding of the formation of a passivation layer on graphite anodes in Li-ion batteries has been undertaken with the goal of improving both high temperature storage, low temperature discharge, and cycle life. This understanding has led to the development of new electrolytes that replace carbonate solvents with water and allow for a wide operating window (>3V) and new Li-ion chemistries. This promises to make Li-ion batteries safer and cheaper.

#### 2.1.4 Lithium-Ion Capacitors

Li-ion capacitors are a hybrid technology that incorporate hard carbon Li intercalation anodes and activated carbon electric-double layer capacitor cathodes. This technology is just being explored as a commercially viable technology that can provide high power and long life at moderate energy density (10 Wh/kg). The current focus for Army applications is to develop improved high temperature storage and lifetime through the incorporation of advanced electrolytes. The use of additives to both improve anode passivation (life) and high voltage stability (energy) if successful can lead to a wider adoption of this technology for embedded applications. The development of hybrid cathode systems, where a relatively small percentage of LiFePO<sub>4</sub> is incorporated with the activated carbon cathode promised higher specific energy (25 Wh/kg), which has wide applications in the Army.

#### 2.2 Electrochemical Energy Conversion

A number of electrochemical energy conversion technologies have been developed to either convert fuels directly to electrical energy (fuel cells) or to convert other forms of energy (JP8, solar,  $CO_2$ ) into fuel. This effort has traditionally been focused on fuel cells, but recent focus has shifted to harvesting energy locally to convert to simple fuels for later use.

#### 2.2.1 Fuel Cells

A significant effort has been undertaken by the Army to develop fuel cells for Soldier and Army vehicle applications. The Soldier application targets 10's of watts at specific energies greater than available in traditional batteries. The vehicle efforts, targeting 100's of watts, have been directed towards auxiliary power units (APU) that can be used to power electronics during Silent watch where operation of the engine would be inefficient and unwanted. Several different technologies have been investigated including proton exchange membrane (PEM) fuel cells using reformed methanol or chemical hydrides to generate hydrogen as fuel and direct methanol fuel cells (DMFC). For Soldier carried systems, the challenge has been to provide 20W in a package comparable in size and weight to a conventional battery.

#### 2.2.1.1 Reformed Methanol Fuel Cell

The reformed methanol fuel cell uses a PEM fuel cell stack that has been shown to operate for 1000's of hours without degradation, so the power generating component of the device is not an issue. The challenge has been to provide hydrogen in a compact and lightweight form. Methanol is such a compact source of hydrogen, but it requires a conversion process to generate the usable hydrogen. To accomplish this, there is a fuel processing system (reformer) that takes methanol and water, and through a series of reactions at 300°C generates H<sub>2</sub> and CO<sub>2</sub>. The CO<sub>2</sub> is exhausted and the H<sub>2</sub> is then used in the PEM fuel cell to generate power. The reformer, fans, pumps, and other controls all encompass the balance of plant (BOP) that make up the bulk of the device. The PEM fuel cell stack itself is a small component of the overall unit. The fuel cell unit also requires a battery for start-up and load leveling. The result is that the reformed methanol fuel cell is a complex device that is costly and difficult to operate for extended periods in fielded conditions. A second approach to generate hydrogen is through the use of chemical hydrides such as LiH, NaBH<sub>4</sub>, or AlH<sub>3</sub>. These materials are typically 10% by weight  $H_2$  and are therefore dense sources of  $H_2$ . There is also a fuel processing step that in the case of LiH and NaBH4 involves reaction with water; in the case of AlH<sub>3</sub>, the addition of heat. Control of the reaction is the challenge here along with storage of the H<sub>2</sub>

generated. This requires a BOP and therefore the specific energy is reduced. The  $AlH_3$  system is the most promising as control of the  $H_2$  generation is easier and the yield is excellent.

#### 2.2.1.2 Direct Methanol Fuel Cell

Direct methanol fuel cells (DMFC) use similar technology to  $H_2$  fuel cells, but operate at lower temperatures (60°C) than the reformed methanol system. The methanol is used directly, and because it is harder to oxidize than  $H_2$ , the resulting energy efficiency is lower. Crossover of the methanol in the cell also results in oxidation of the fuel without useful energy being produced, and this further reduces efficiency. The system is beneficial for carried applications because of its lower operating temperature and overall energy density in the finished fuel cell unit. The DMFC also has a BOP that is used to dilute the methanol, as it cannot be used at 100% concentration, and to recycle water in the system. Soldier carried systems have been developed with the required 20W power, but due to cost and complexity, have not been adopted.

### 2.2.1.3 Reforming Battlefield Logistics Fuel for H<sub>2</sub>

Reforming the fuel used by most Army vehicles to produce  $H_2$  for PEM fuel cells has been an Army specific approach to incorporating fuel cells on the battlefield. Reforming JP8 requires first removing the sulfur compounds using absorbent materials, and then developing reformation catalysts that are tolerant to low (10 ppm) residual levels of sulfur. This effort has been to develop new materials with high capacities to trap organosulfur compounds from the fuel stream, and to re-use the absorbent after a regeneration (heating) step. The efforts have resulted in sulfur absorbent materials that are 5 times better than conventional materials. A second effort in this area has focused on developing a microns thick supported palladium (Pd) membrane for separating  $H_2$  from other byproducts of the JP8 reformation process. Utilizing cleanroom technology, ARL has been successful in developing this Pd membrane that supports the high rates of  $H_2$ diffusion for practically relevant separation conditions. This membrane has a small fraction of the Pd found in conventional Pd membranes with significantly faster  $H_2$ transport.

### 2.2.1.4 Hybrid Acid-Alkaline Fuel Cells

The benefit of a hybrid acid-alkaline fuel cell utilizing methanol as fuel is significantly reduced BOP. The hybrid acid-alkaline fuel cell efforts have three components, design of the fuel cell system with modeling calculations on the concentrations of reactants and products ( $CO_2$  and  $H_2O$ ) under different operating configurations and conditions. This

effort has led to the conclusion that a bipolar membrane cell should function with less water management required and therefore less BOP than conventional DMFC's resulting in a more compact system. Additional work has been done to develop membranes that can operate for extended periods in alkaline conditions. There has been both internal and external efforts in this area with ARL evaluating materials produced by external partners. There has also been an effort to develop new non-precious metal catalysts that can be used in alkaline conditions which will result in lower cost systems as platinum is now the typical cathode catalyst.

#### 2.2.1.6 Sunlight to H<sub>2</sub>

There are several approaches being considered to convert readily available waste streams in the field to usable fuel for generators or fuel cells. Urea and grey water can be remediated and simultaneously,  $H_2$  can be produced to be used as fuel or to facilitate production of small molecule fuels.

#### 2.2.1.7 CO<sub>2</sub> to Fuel

The Army uses significant amounts of JP8 on the battlefield. This generates large volumes of  $CO_2$  gas. This effort is designed to convert waste streams ( $CO_2$ ,  $H_2O$ ) from field generators to liquid fuel by harvesting solar energy. In order to accomplish this, new catalysts are being designed and evaluated that convert  $CO_2$  and water into small molecule fuels such as  $CH_4$ ,  $CH_3OH$ , and HCOOH, which can then be used directly or upgraded to longer chain hydrocarbons. The use of membrane cells that take advantage of separating the products of of  $CO_2$  reduction from the counter electrode reaction are also being investigated to improve efficiency and lower recombination in these systems. This effort focuses on development using catalysts and solar absorbers.

#### 3. Summary

An overview of some of the development work being carried out in the Electrochemistry Branch is given. These material and system development efforts are supported by fundamental research in electrolyte interfaces, electrolyte structures, the interaction of light with nanostructures to produce catalytic effects, as well as extensive computational modeling of these same systems from the molecular to the macroscopic device level. The research areas are more comprehensive than given here, but this sampling will serve as an orientation into the research and as an introduction for the next several chapters in this book.

## Chapter 1

# **Recent Trends in Double Layer Capacitors and Dual Intercalation Batteries from Molecular Prospective**

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#### Abstract

Supercapacitors or electrical double layer (EDL) capacitors store charge *via* rearrangement of ions in electrolyte and their adsorption on electrode surfaces. They are actively researched due to multiple potential applications requiring longer cycling life, broader operational temperature range, and higher power density compared to batteries. Recent developments of nanostructured carbon-based electrodes with high specific surface area have demonstrated the potential to significantly increase supercapacitor energy density. Molecular modeling of electrolytes near charged electrode surfaces has provided key insights into fundamental aspects of charge storage at nanoscale, including an understanding of the mechanisms of ion adsorption and dynamics at flat surfaces and inside nanopores, and the influence of curvature, roughness, and electronic structure of electrode surfaces. Here we review these molecular modeling findings together with available experimental observations and put this analysis into perspective of future developments in this field. Current research trends and future directions are discussed.

#### Keywords

Battery, Capacitor, Molecular Dynamics Simulations

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#### 1. Introduction

The increasing demand for efficient, reliable and affordable energy storage devices stimulated research into the Faradaic and non-Faradaic phenomena occurring at the electrode-electrolyte interfaces. In the Faradaic devices, such as batteries or pseudocapacitors, the charge is stored due to electrochemical reactions occurring at electrodes. In contrast, capacitors store energy via non-Faradaic processes (i.e., involving physical phenomena without chemical reactions). Depending on the type of materials and charge storage mechanisms involved there are three types of capacitive storage devices: dielectric capacitors, electrolytic capacitors and electric double layer capacitors (EDLCs) or supercapacitors.<sup>1, 2</sup> In dielectric capacitors, the space between electrodes is filled with a dielectric material and the energy storage involves reorientation of material local dipoles such that they oppose the externally applied electrostatic field between the plates. These capacitors have the fastest charge-discharge rate, operate at high voltages (kV) and in alternating current. However, the stored energy normalized per mass of dielectric material in this type of capacitors is small, as shown in Figure 1. The energy density of dielectric capacitors can be increased by the utilization of dielectrics with high electric permittivity or ferroelectrics, e.g., the class II ceramic capacitors. <sup>3, 4</sup> The electrolytic capacitors are comprised of two metal electrodes, typically made of aluminum, tantalum or niobium, with ion conducting liquid or solid electrolyte between one of the electrodes and a dielectric material formed by oxidation of the surface of another electrode <sup>5</sup>. These capacitors are commonly utilized in electronics or as power supplies and their current market size exceeds US\$6 billions/year.<sup>1, 6, 7</sup> Among the disadvantages of electrolytic capacitors are their relatively short lifetime and large leakage currents.



*Figure 1. Ragone plot illustrating the power versus energy density for various electricity based energy storage devices. Figure 1 is based on data compiled from several sources.*<sup>24, 152-157</sup>

The EDLCs, on the other hand, are usually comprised of porous electrodes and liquid electrolyte. The charge storage is achieved *via* double layer restructuring due to applied electric field causing the ion diffusion and adsorption at the electrode surface. As the energy in EDLCs is stored within this thin interfacial layer, the enhancement of the energy density arises primarily from the increased specific surface area (SSA) of porous electrodes. Activated carbon is one of the most currently used electrode materials made by charring and partially oxidizing the precursor using steam or carbon dioxide to create or enhance nanoscopic pores, often followed by subsequent purification to reduce impurities. While coconut shell activated carbon and \$15 per kg for the EDLC-grade carbon in 2013) material that has been considered as the most common for practical applications

in EDLCs, other natural precursor derived activated carbons<sup>8, 9</sup> as well as more advanced C-based materials have been widely investigated by academic groups.<sup>8, 10-12</sup> Extensive experimental work focusing on understanding and design of nanostructured materials for energy storage applications allowed an increase in SSA of C-based porous electrodes from a few hundreds  $m^2/g$  in powders or activated carbons to 2000-3500  $m^2/g$  in various carbide-derived carbons (CDC), C-onions, zeolite or silica or alumina-templated carbons, Kroll carbons, graphene, polymer-derived carbons, vertically aligned C-nanotubes, aerogels, nanotubes and carbon-fibers.<sup>2, 8, 11, 13-22</sup> Recent research showed that it is technically possible to synthesize porous electrode materials based on 3D-graphenes with SSA as large as  $4000 \text{ m}^2/\text{g}$ .<sup>23</sup> Many of these nanostructured materials, such as nanotubes or 3D-graphenes, unfortunately, have a low packing density resulting in low volumetric energy density.<sup>24</sup> The low volume density electrode materials increase the amount (and hence the weight and cost) of inactive components present in EDLCs such as bulk electrolyte, current collectors, separator, binder, connectors, and packaging therefore making such low-density electrodes much less attractive for assembly of thin electrode cells.<sup>10, 24</sup> Hence, both volumetric and gravimetric energy densities as well as electrode thickness need to be considered as performance metrics in addition to the commonly considered values of capacitance per unit surface area or per mass of electrode material.

In comparison with dielectric and electrolytic capacitors, the EDLCs with highly porous electrodes achieve the highest non-Faradaic capacitance and charge/energy density<sup>25</sup> making them suitable for applications requiring intermediate power density over longertime discharge, e.g., emergency doors, memory backups, car starters, detonators, pulsed lasers, pacemaker devices, defibrillators, electric forklifts, cranes, and even electric buses and trains.<sup>10</sup> Almost half of today's supercapacitor production is designated to electric vehicle transportation (EVT).<sup>26</sup> In EVT, the addition of supercapacitors to electrochemical batteries or fuel cells enables regenerative braking and faster acceleration, increases the overall energetic efficiency up to 20-25% and improves the life-time of batteries.<sup>27, 28</sup> EVT based exclusively on supercapacitors (or the so called capa vehicles) was already tested as a non-polluting and energy efficient alternative for inner-city transportation that requires multiple stops (where recharging could be done in as little as half a minute) and relatively short distances (few miles) between stops. Such supercapacitor-only based EVT apparently is 20-50% more energy efficient than overthe-line electric vehicles (trolleys, electric trains).<sup>29</sup> EDLCs are also utilized in the bridge power applications, where immediate power availability may be difficult to achieve, such as in Uninterruptable Power Supply (UPS) systems utilizing generators, fuel cells or flywheels as the main power backup. The EDLC burst power applications are still limited to frequencies lower than 100 Hz and often sacrifice the energy density to

increase the power density.<sup>30</sup> The supercapacitors could also be ideal for storing relatively small amounts of solar, mechanical, and thermal energy harvested from (relatively small) environmental energy fluxes.<sup>31-33</sup> For example, traffic speed indicators or video cameras could be powered by a combination of solar cells and supercapacitors. The supercapacitors can be scaled to any desired size from nano/micro-meter in electronics to locomotive/wagon size (of tens of tons) in railroad transportation.

Because of the inherent advantages of the reversible charge storage, it is expected that the demand for non-Faradaic energy storage will increase in the near future. Specifically, it is projected that the supercapacitor market will rise from about US\$1 billion per year today to several billions in the next decades.<sup>7, 29</sup> However, the larger scale deployment of supercapacitors will depend on how the current and future research addresses their shortcomings which will be discussed in the next sections.

The EDLC electrolytes are usually based on aqueous or organic based solvents, such as propylene carbonate (PC) or acetonitrile (AN), while room temperature ionic liquids (RTILs) are currently investigated as a promising nonflammable alternative for higher temperature, higher voltage applications.<sup>8</sup> Electrolytes with protic solvents at typical salt concentrations (0.1-3M) suffer from narrow electrochemical stability window, but offer higher conductivity and could be advantageous in high rate applications. On the other hand, it was recently demonstrated that super-concentrated aqueous solutions of Li-salts (~20m for single salt and up to 27m for a mixture of two salts) can increase the operational potential window slightly above 3V due to the suppression of the hydrogen/oxygen chemical evolution at electrodes.<sup>34-37</sup> Aprotic solvents have the intermediate stability and rate characteristics between aqueous electrolytes and RTILs, but may operate at extremely low temperatures down to -70 °C.<sup>38</sup> The RTILs consist of relatively bulky organic ions that are liquid at room temperature. They yield acceptable ionic conductivity and viscosity, low vapor pressure, low toxicity and low flammability, which makes them attractive candidates for EDLCs if their cost can be reduced.<sup>39,40</sup> Also, a wide variety of possible chemical structures of cations and anions suitable for RTILs allows for further chemical tailoring of these liquids to obtain the desired properties. In some cases, addition of an aprotic solvent to RTIL is useful because the solvent can decrease the viscosity, increase the mobility of ions, and extend the lower end of the operating temperatures. Usage of asymmetric (in size and shape) ions or mixtures of ionic liquids also provided a viable strategy for extending the liquid range to lower temperatures beyond the melting point of traditional solvents.<sup>41</sup>

Unlike continuous double layer formation occurring in EDLC with increasing voltage, the anion insertion into graphite occurs at well-defined potentials, typically around 4-5 V vs.  $\text{Li/Li}^+$ . Such anion intercalation expands the graphite interlayer spacing to dimensions

comparable to the smallest pore sizes used in EDLC, giving rise to some similarity between them as we discuss below. Due to a well-defined anion intercalation potential that is analogous in many ways to the lithium intercalation in graphite, devices relying on both anion and cation Faradaic reactions are classified as a dual-ion battery. In addition to dual-ion batteries with all-carbon electrodes, alloyed anodes could replace graphite negative electrodes leading to a further increase in the energy density of dual-ion batteries. Some of the challenges of the dual-ion battery (DIB) are a relatively low volumetric capacity experimentally observed in the graphite cathode and the need to identify electrolytes that are compatible with the relatively high cathode voltages (4-5 V vs Li/Li<sup>+</sup>). DIBs exhibit energy densities higher than EDLC capacitors but lower than lithium ion batteries (LIB) as shown in Figure 1. DIB energy density is determined by the capacity of electrodes, voltage between electrodes and ability of electrolyte to provide both lithium cations and anions for intercalation into anode and cathode. Thus, it is important to choose electrolytes with high salt solubility and conductivity over wide concentration range in addition to ensuring that electrolyte in electrochemically compatible with both electrodes. Unlike DIB, current lithium-ion batteries (LIBs) rely on shuttling lithium ions between graphite negative anode and intercalation cathode. LIB energy density is largely determined by electrode capacities and voltage between electrode after accounting for the weight of electrolyte, current collectors, separator and packaging. Current lithium-ion batteries are cathode limited, similar to DIBs, and require electrolytes to be either electrochemically stable at these potentials or form a stable ionically conducting and electronically insulating passivation layer to kinetically protect electrolyte from further redox reactions at the electrodes. A high gravimetric and, especially, high volumetric capacity and voltage of lithium-ion battery cathodes such as lithium cobalt oxide and lithium nickel cobalt manganese oxide yield high energy densities for lithium-ion batteries (see Figure 1) when paired with graphite or alloyed anodes, making lithium-ion batteries the technology of choice for portable electronics, hybrid and electric vehicles, and power tools.<sup>42</sup>

In EDLCs and DIBs devices discussed above, the molecular scale phenomena are key in controlling the performance and design strategies. These phenomena include: i) more efficient packing of ions in EDL or inside pores at lower voltages to increase capacitance; ii) role of quantum capacitance to ensure that it is not a limiting factor; iii) faster transport of ions inside the pores; iv) intercalation kinetics for faradic devices; v) improved electrochemical stability of electrolytes to expand electrochemical window or to control the passivation layer for hybrid devices; vi) design of hybrid micro and macro-pores architectures to optimize transport and capacitance. Below we will discuss these

molecular scale phenomena and their influence on the efficiency of energy storage devices.

#### 2. Structural properties of electric double layer

In this section, we discuss recent theoretical and experimental advances in understanding the structure of the electrode-electrolyte interface, the EDL capacitance, and the energy density stored by various electrolytes at different electrode structures. We reiterate that the energy/charge stored by the capacitor can be quantified with the integral capacitance  $(C_I)$ . The  $C_I$  is defined as the ratio between the electrode charge  $\sigma$  (normalized either per unit specific surface area (SSA) or mass of the electrode) and the applied potential  $\Delta U$ between electrodes,  $C_I = \sigma/(\Delta U/2)$ . For characterization of the electrode-electrolyte interface and the sensitivity of its properties to the electrode potential, the differential capacitance  $(C_D)$  defined as the derivative of the electrode charge with respect to electrode potential,  $C_D = d\sigma/dU_{electrode}$  is commonly used both in experiments and modeling. The electrode potential  $(U_{electrode})$  is readily available from simulations by integrating the Poisson equation of the ensemble averaged charge distribution from the electrode surface to bulk electrolyte.

The fundamental understanding of  $C_I$  and  $C_D$  magnitudes and their dependence on voltage, temperature, and the chemical structure of electrode and electrolyte is key to elucidating correlations between the structural changes within the EDL and routes to achieve capacitance enhancement. For example, in light of simple EDL models<sup>43</sup> one would associate the increase of capacitance upon increasing the electrode potential with low concentration of ions near the electrode surface. In contrast, a decrease of capacitance as the electrode is charged can be caused by ion crowding and oversaturating at the surface. Also, sharp peaks in  $C_D$  at certain voltages can indicate possible phase transitions within the interfacial layer.

As an electric field (or charge) is applied on the electrode, the ionic electrolyte will restructure such that it will diminish (or screen out) the impact of the applied field. Extensive experimental work based on atomic force microscopy and theoretical work based on MD simulations showed a consistent picture regarding the EDL structure formed at the electrode-electrolyte interface. Specifically, in pure RTIL and concentrated electrolytes, the layers locally rich either in counterions or coions are forming near the surface along the direction perpendicular to the electrode surface. It is quite remarkable that the AFM experiments reached a level of resolution that can accurately pinpoint individual electrolyte layers near the electrode surface.<sup>44</sup> This EDL structure generates space charge oscillations in the electrolyte, as exemplified in Figure 2. For pure RTILs it is often the case that the innermost electrolyte layer near the surface (about 5-6Å width