On the Cover (from left to right):

1. Cell design for flow batteries. (see V.K. Gattu, page 15);

2. Nyquist impedance plot of bare silicon measured at 100°C. (see M. Saber et al., page 3);

3. Emission due to car exhausts. (see M. Patel, page 20).
Journal of Undergraduate Research

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Founding Editor: Robert F. Klie

Department of Physics
University of Illinois at Chicago
845 W Taylor Street, M/C 273
Chicago, IL 60607
email: rfklie@uic.edu
312-996-6064

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## Contents

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>v</td>
</tr>
<tr>
<td>R.F. Klie</td>
<td></td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>vi</td>
</tr>
<tr>
<td>Electrochemical Impedance Spectroscopy and Characterization of 20% Yttria doped Cerium on Silicon</td>
<td>1</td>
</tr>
<tr>
<td>M. Saber, J.I. Rossero, and C.G. Takoudis</td>
<td></td>
</tr>
<tr>
<td>A Look at Some International Lithium Ion Battery Recycling Initiatives</td>
<td>5</td>
</tr>
<tr>
<td>A. Mancha</td>
<td></td>
</tr>
<tr>
<td>Combined Heat &amp; Power's Role in Modern Grid System</td>
<td>8</td>
</tr>
<tr>
<td>J. Jiang</td>
<td></td>
</tr>
<tr>
<td>Flow Batteries - Storing Energy on the Grid</td>
<td>12</td>
</tr>
<tr>
<td>V.K. Gattu</td>
<td></td>
</tr>
<tr>
<td>Combined Heat &amp; Power: CHP Present &amp; Future</td>
<td>17</td>
</tr>
<tr>
<td>M. Patel</td>
<td></td>
</tr>
<tr>
<td>Short Term Energy Storage on Grid</td>
<td>21</td>
</tr>
<tr>
<td>S.E. Kazokoglu</td>
<td></td>
</tr>
<tr>
<td>Electric Vehicle Batteries: Li-ion and Beyond, Challenges and Advancements</td>
<td>25</td>
</tr>
<tr>
<td>B. KC</td>
<td></td>
</tr>
</tbody>
</table>
Introduction

Dear Readers,

welcome to the ninth edition of the Journal of Undergraduate Research at the University of Illinois at Chicago, largely devoted to papers for the LAS 493 course on Energy Storage for the Grid and Transportation in Fall 2015. For the first time in its nine year history, we had enough submissions to the journal to fill two issues this year. We hope to continue this trend in the coming years.

The first 7 papers discuss a variety of topics, ranging from electrochemical measurements of mixed valence oxides to advanced batteries beyond Li-ion. We hope that you enjoy the various reviews, as well as the original scientific discussions contained in this issue.

At this point I want to thank the National Science Foundation (DMR-1408427) for the financial support to keep the journal going, as well as Nicholas Gross for all his hard work in editing the manuscript for the journal.

Robert F. Klie
University of Illinois at Chicago

October 2016
Acknowledgements

We would like to acknowledge support for this publication from the National Science Foundation (Grant No. DMR-1408427). Also, we would like to thank Nicholar Gross for his help with typesetting this issue of the Journal of Undergraduate Research.
Electrochemical Impedance Spectroscopy and Characterization of 20% Yttria doped Cerium on Silicon

Muna Saber, Jorge I. Rossero, and Christos G. Takoudis

Department of Chemical Engineering, University of Illinois at Chicago, Chicago, IL

Bare silicon and 20% yttria stabilized ceria on a silicon substrate are annealed. The annealed substrates are analyzed at varying temperatures using electrochemical impedance spectroscopy. The impedance data is fitted against appropriate equivalent circuits and the fitted data is characterized with an Arrhenius plot and a plot of the ionic conductivity against temperature. The 20% YDC sample is found to have a high ionic conductivity, and therefore should be studied further in order to determine the practicality of using YDC as an electrolyte.

Introduction

Solid Oxide Ceramic Fuel Cells, or SOFCs, are devices that produce energy through oxidizing a fuel. SOFCs have three main components: an anode, a cathode, and an electrolyte. In the cathode, an oxidant, generally oxygen from air, is continuously fed to the cathode and reduced. The oxygen ions travel through the electrolyte to the anode. In the anode, continuously added fuel is oxidized with oxygen ions entering through the electrolyte. Electrons from the anode are transported to the cathode in order to drive the process. SOFCs generally operate at high temperatures of approximately 1000 °C. Lowering the operating temperature of the SOFC would reduce the operating costs and degradation rate of SOFCs, making their use more reasonable.

In order to increase the performance of SOFCs, the components should be optimized. For example, the cathode and the anode of the SOFC should have high electrical conductivity in order for ions to be driven through the electrode. The cathode should be porous in order to allow oxygen molecules to enter the electrode. Therefore using porous materials with increased ionic conductivity can be used in order to increase the performance of the cell. A porous material needs to be used for anode as well as this would allow fuel molecules to enter.

For the electrolyte, the material is an ionic conductor in order to facilitate the transport of negatively charged ions. The electrolyte should also have a low electronic conductivity in order to reduce electricity losses through the electrolyte. Grain boundaries, interfaces between separate grains in crystalline structures, decrease the rate at which ions can travel through an electrolyte, as there is a higher resistance at the grain interfaces than the interior of the grain. Because the grain boundary resistivity hinders the movement of oxygen ions, the grain boundary resistivity should be low.

A widely used and studied electrolyte material is yttria stabilized zirconia (YSZ) as a result of its high ionic conductivity and low electronic conductivity. In this material \( \text{ZrO}_2 \) molecules are stabilized with the addition of \( \text{Y}_2\text{O}_3 \). Another much less studied material is yttria doped ceria (YDC). This is created by adding \( \text{Y}_2\text{O}_3 \) to \( \text{CeO}_2 \) in order to increase the electrolytes ionic conductivity.

For solid electrolytes, the conformation of the solid impacts the ionic conductivity. This concept is the building block behind the use of YSZ as an electrolyte. At room temperature, \( \text{ZrO}_2 \) holds a monoclinic structure. In a monoclinic structure, ions have the ability to travel through the material in multiple directions and each path has a different length. This structure is inefficient as the ions may, as a result, go through longer paths in order to travel through the electrolyte. If \( \text{Y}_2\text{O}_3 \) is added to the \( \text{ZrO}_2 \), the zirconia may be stabilized into the cubic or tetragonal structure. These structures are more favorable as they lessen the distance that the ions need to move. For the cubic structure, all the directions that the ion may travel have sides of equal length. This lessens the overall distance that ions travel and is the reason that Yttria Stabilized Zirconia is used rather than pure \( \text{ZrO}_2 \).

Another material that may be used as an electrolyte is yttria doped cerium (YDC). At the operating temperatures of an SOFC, cerium has a cubic structure and does not need \( \text{Y}_2\text{O}_3 \) for stabilization. \( \text{Y}_2\text{O}_3 \) is added to the ceria in order to increase the electrolyte’s ionic conductivity. \( \text{Y}_2\text{O}_3 \) causes oxygen vacancies to develop. These vacancies allow a larger amount of oxygen ions to pass through the YDC matrix.

In our experiment we will be furthering research on YDC as a possible electrolyte by testing the electrochemical properties of YDC. The impedances of bare silicon and YDC on silicon will be examined in order to understand which effects originate from YDC and which originate from Silicon. From this data, the relationship of the resistivity and ionic conductivity with temperature can be determined.

Methods

Impedance Spectroscopy

Electrochemical impedance spectroscopy is used in the measurements and analysis of materials for which ionic conduction dominates. Using an applied potential, the
impedance is measured and analyzed. The method with which the electrolyte is measured depends on the phase and properties of the electrolyte. For solid electrodes, impedance is measured using two parallel electrodes on the same plane. The response of the can then be displayed and analyzed with analytical software. The response is plotted on a three dimensional plot with axes of the log of frequency, the real impedance and imaginary impedance. This three dimensional plot can then be separated into a Bode impedance plot and a Nyquist Impedance plot. The impedance data can then be analyzed and fitted to an Equivalent circuit, dependent on the examined material.

**Experimental Setup**

A 100 nm sample of bare silicon doped with boron is annealed at 700°C for 10 minutes under flow of helium and then cooled to room temperature. Two parallel electrodes are pasted onto the sample using high temperature silver paste (Heraeus C8729- conductor paste). Immediately after annealing each sample, the impedance of the sample is measured using electrochemical impedance spectroscopy (EIS). The sample is placed in an enclosed chamber and the impedances are measured with a potentiometer. The impedance of the samples are measured at room temperature and then the temperature is incrementally increased to 600 °C.

Yttria doped ceria films are deposited on silicon using the precursors tris(isopropyl-cyclopentadienyl) Cerium maintained at 120 °C , and tris (isopropyl-cyclopentadienyl) Yttrium maintained at 110 °C as well as water vapor. Six silicon substrates were cut into 1.5 cm by 1.5 cm squares and cleaned. The cleaned samples are placed in the reactor chamber and the metal precursors are added into the reactor.

Six samples of 45 nm 20%YDC on 100nm samples of silicon doped with boron are annealed at 700°C for 10 minutes under flow of helium and cooled to room temperature. After annealing each sample, the samples were analyzed with electrochemical impedance spectroscopy using a Bio-Logic SP-240 potentiostat. 10 mV AC digital amplitude is used. The sensors are placed on the sample using high temperature silver paste. The impedances are measured at room temperature and as the temperature is incrementally increased to 600°C.

The impedance data is recorded and analyzed using E.C. lab, an EIS software. The Nyquist impedance and Bode impedance plots are then fitted against an equivalent circuit so that the sample may be analyzed. The Bode Impedance plot is a graph of the absolute value of impedance and the phase of the impedance with respect to the frequency. The Nyquist impedance plot shows a graph of the imaginary impedance plotted against the real impedance.

**Determining the Equivalent Circuits**

For the impedance plots of each sample to be analyzed, they can be fitted against an appropriate equivalent circuit. The equivalent circuit used to fit the Bare Silicon Impedance plots is shown in Figure 1, where R1 and R2 represent resistors and C1 represents a capacitor. The R1 represents the resistivity resulting from the potentiometer. The R1/C1 section represents interfacial diffusion of oxygen molecules.

![FIG. 1: Equivalent Circuit of Bare Silicon](image1)

The equivalent circuit of 20% atom YDC on silicon has to include the effect of the grain boundary resistivity throughout the electrolyte as well as the effect of oxygen ions transporting through the YDC. The resulting equivalent circuit is shown in Figure 2, where R1, R2, R3, and R4 are resistors; C1,C2 and C3 are capacitors; and Q1 is a constant phase element. R1 represents the effects of the potentiostat and (Q1+C2/(R3)) represents the effects of the grain boundary. C1/R2 represents the interfacial oxygen diffusion on the face of the electrolyte and C3/R4 represents the movement of oxygen ions through the YDC matrix.

![FIG. 2: Equivalent Circuit of 20% YDC on Silicon](image2)

**Results and Discussion**

**Silicon Impedance Trends**

After the impedances of the bare silicon samples at differing temperatures were recorded, they were fitted against the stated equivalent circuit. The fits were found to be accurate representations of the experimental data as shown in Figure 3. No grain boundary is present.

When the Nyquist plots of bare silicon samples of differing temperatures are compared, as shown in Figure 4, two trends transpire. From 100 °C to 300 °C the impedance of the samples decrease and from 350 °C onward the impedance increases.
FIG. 3: Nyquist impedance plot of bare silicon measured at 100 °C. The red points correspond to the fit created by the equivalent circuit while the blue points correspond to the experimental data.

FIG. 4: Fitted Nyquist Impedance plots for Bare Silicon tested from 100 °C to 400 °C.

The change in the relationship between temperature and impedance for the samples is likely a result of boron doped silicon acting as a semiconductor.

20% YDC Characterization

After the impedances of 20% YDC on silicon at differing temperatures is recorded, the plots were fitted to the stated equivalent circuit. The fits were found to be accurate as shown in Figure 5. The grain boundary resistivity is suggested by the graph as there are two maxima in the Nyquist plot. The first maxima corresponds to the grain boundary resistivity.

The ionic conductivity of each 20% YDC sample was plotted against temperature. The equation used to find the conductivity at each temperature is

$$\sigma = \frac{d}{S \cdot R},$$

where $\sigma$ is the ionic conductivity at a certain temperature, $d$ is the thickness of the sample, $S$ is the surface area of the sample, and $R$ is the total resistance calculated through the equivalent circuit.

The data is plotted against temperature and fitted to an exponential function in Figure 6. The equation of the fitted plot is $y = 2 \cdot 10^{-14} e^{0.0277x}$. The surface area of the sample is 1.62 cm and the thickness of the sample is 40 nm.

The ionic conductivity is a key property for electrolytes and therefore the trend for the increase of Ionic conductivity with increasing temperature must be understood. A good electrolyte must have a high Ionic conductivity. Thus this relation can be used to determine the approximate Ionic conductivity of the electrolyte at SOFC operating temperatures and to compare 20% YDCs Ionic conductivity with other material when choosing an appropriate electrolyte.

Arrhenius Plot

The Arrhenius plot of the 20% YDC samples was plotted against 1000/Temperature as shown in Figure 7. The equation for the Arrhenius plot is

$$\sigma T = A \times e^{\frac{-E}{kT}},$$

where $E$ is the activation energy, $k$ is the rate constant, $T^*$ is absolute temperature and $A$ is a pre-exponential factor. The linear regression equation for the data from 373 K to 523 K is $-0.244T - 6.208$. The linear regression equation for the data from 573 K to 673 K is $-3.827T + 1.695$.

The linear regression used to fit the data of the Arrhenius plot changes after 523 K. The reason for this change
FIG. 6: Graph of the total ionic conductivity of 20% YDC samples against temperature. The diamond markers are the calculated data. The black line corresponds to the fitted exponential plot.

is that, as stated earlier, the impedance of the silicon base, which is contingent on the resistivity, has a changing correlation with temperature. The conductivity of a material is directly calculated from the resistivity system. Therefore the linear regression must be changing where the relation between impedance and temperature changes. According to the Nyquist Impedance graphs, this change occurs between 523 K and 573 K.

FIG. 7: Arrhenius plot for 20% YDC samples from 373 K to 673 K. Blue points correspond to the calculated data. The red line corresponds to the linear regression for 573K to 673K and the light blue line corresponds to the linear regression for 373 K to 523 K.

Conclusion

The experimentally collected impedance spectroscopy data for YDC on silicon and bare silicon was fitted using equivalent circuits dependent on the properties of the samples. These equivalent circuits accurately represented the experimental data. The fitted Nyquist Impedance plots for bare-silicon showed that Impedance decreased with the T from approximately 100 °C to 300 °C and then began increasing with temperature.

For YDC, the ionic conductivity increases with temperature. The relationship for ionic conductivity and absolute temperature can be modeled with an exponential function. The Arrhenius plot showed a change in behavior near 300 °C from a small slope to a steeper slope.

Acknowledgements

The author would like to thank Dr. Gregory Jursich, Xiaodan Cui, Arman Butt and John Grotberg for providing assistance in theoretical concepts on ALD and equivalent circuits.a

4 Structure and phase relationship of cubic zirconium dioxide (1975).
6 M. Krauz, M. Radecka, and M. Rękas, Materiały Ceramiczne 63, 157 (2011).
Today the United States is heavily reliant on the lithium-ion battery as most portable devices and electronics run on it. Current innovations are also looking on how to maximize it on the grid and transportation. This paper will look at three sovereign states and their current initiatives on Li-ion battery recycling: US, European Union, and China. The term initiative is used loosely as the information is not permanent in most policies or plans. Li-ion battery recycling initiatives are crucial to look at because used and wasted Li-ion batteries can disrupt public health and Li-ion batteries are expected to be a factor for effective material supply for future battery production especially in transportation, like the Tesla Roadster.

**Introduction**

The digital revolution is the shift from analog technology to digital technology. The Internet and the continuous use of electronics can characterize it. Most personal electronics are portable and run on lithium ion batteries. Portable electronic devices, like the laptop, have given people easy access to connect to each other anytime, anywhere. The Internet has given birth to a new form of communication through social media and a new way for data collection and record keeping. With the age of sustainability and the marketability of greener products from media like Youtube, consumers are shifting to buy products like hybrid cars and organic food. Due to this, the consumer demand for lithium ion batteries has increased dramatically.

In 2012, about 27% of the global lithium consumption came from rechargeable batteries while it was only 15% in 2007 and only 8% in 2002. The world lithium consumption from 2000 to 2008 had a steady 10% rate increase. According to signumBOX, the demand for energy storage and transportation will have at least a projected 20% annual growth rate until 2025. Table I shows the breakdown.

<table>
<thead>
<tr>
<th>Application/Tonnes Lithium Carbonate Equivalent (LCE)</th>
<th>2011</th>
<th>2025</th>
<th>CAGR 2011-2025</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batteries for Portable Devices</td>
<td>30,416</td>
<td>111,176</td>
<td>9.7%</td>
</tr>
<tr>
<td>Batteries for Grid</td>
<td>500</td>
<td>7500</td>
<td>21.3%</td>
</tr>
<tr>
<td>Batteries for EV and Hybrid</td>
<td>6967</td>
<td>204,901</td>
<td>27.3%</td>
</tr>
<tr>
<td>Other</td>
<td>91,400</td>
<td>174,904</td>
<td>4.7%</td>
</tr>
<tr>
<td>Total Li Demand</td>
<td>129,283</td>
<td>498,571</td>
<td>10.1%</td>
</tr>
</tbody>
</table>

Some estimates suggest that by 2020, electric vehicles with lithium batteries are more likely to account for most electric vehicles. Consequently, questions about lithium consumption and availability of these batteries have slipped into energy conversations in recent years. This paper will present and summarize some current international initiatives surrounding battery recycling, and if possible lithium ion batteries in the US, Europe, and China. It is important to look at these initiatives as it concerns the growing number of wasted and unused batteries, which in the future will most likely be lithium ion batteries. While the US, Europe, and China may not agree on how to recycle, the initiatives give an idea of how the wasted batteries will be utilized to avoid a potential health hazard. Having these initiatives allows the world to become accountable for a sustainable path. Europe, USA, and China are simply a few players in this path.

**Lithium Ion Battery Background**

The lithium ion battery is found in many electronic devices. It is favored due to their high energy density, long run time, handle of discharge/charge cycles, and stable power. Lithium is a highly reactive element because it is an alkali metal. It enables technologies that can store large amounts of electrochemical energy. This battery is heat sensitive and extreme heat can induce degradation. On very rare occasions, the battery can burst into flames due to overheating and short-circuiting. Voltage estimation for the Li-ion battery can be established by a sound battery model, which addresses chemical, electrical, and physical properties of the battery and can be used to predict battery performances in different environments. However, the data is experimental and is not necessarily the most precise tool.

With all these consequences, lithium-ion batteries that are tossed in a landfill can be a health concern. The highest level measured in lithium batteries comes from cobalt at 278,000 mg/L with the regulatory threshold for hazardous waste at 8000 mg/L. The research group concluded that the lithium-ion battery is associated with portable electronic products as potential sources of hazardous metal pollutants in the environment particularly...
in regions lacking infrastructure in solid waste collection, sorting, and recycling.\textsuperscript{4}

Most lithium ion battery packs have the same components. They can consist of a metal cylindrical shell, voltage converter and regulator circuit, voltage tap, and a battery charge state monitor.\textsuperscript{5} The metal case holds the anode and cathode. The question of recyclability starts from here and demonstrates some obstacles found from varying manufacturers as how they make it is usually kept under wraps.

**Lithium Ion Recycling Challenges**

Not all recycling processes are created equally. Recycling is useful to alleviate material scarcity, reproduce cheaper materials with old components, reduce energy and emissions, and to create a more sustainable process. With Li-ion batteries, the chemical compositions of the active materials vary and are unstandardized. The common cathode used in consumer electronics is LiCoO\textsubscript{2}, but it is also costly. Other combinations are available and used differently by manufacturers depending on the lower raw material cost.\textsuperscript{6}

Due to this, the best solution may be to allow the processes for recycling tailored to the specific battery type. Along with different solutions for recycling, there are some growing concerns over the availability of lithium. Some demonstrated that the lithium demand can be met and battery material shortages are unlikely assuming that recycling will mitigate the potential scarcity.\textsuperscript{7}

Most of the world’s lithium production is found in Bolivia, Chile, Argentina, and China.\textsuperscript{1} These countries can potentially play a huge role in the market and cycle, especially China since it makes its own Li-ion battery as well.

As far as trading peak oil for peak lithium, the lithium production market is still a fairly new market, so predictions of when peak lithium is reached are premature. Although, the world will reach a peak at some point, even though some may not agree. Recycling lithium and only requiring a fraction of annual use to be mined can avoid it. Even as the lithium reserves and resources increase with the market demand.

Recycling can help each nation to have its own supply without having to rely on other nations.\textsuperscript{5} Of course, each nation has its own plans to deal with wasted batteries, which is why taking a look at their initiatives is important for the long-term goal.

**Europe Initiatives**

In 2006, the European Union set up the Battery Directive, which is meant to regulate and recycle batteries overall. It was created for the European Member States to set up national laws on batteries under Art. 26 due to the approximate 800 tons of automotive batteries, 190 tons of industrial batteries, and 160 tons of consumer batteries of all types entering the European Union each year.\textsuperscript{8} With this, the EU legislation acknowledged the battery waste and holds itself accountable. The Battery Directive is intended for the EU to contribute to the protection, preservation and improvement of the quality of the environment by minimizing the negative impact of waste batteries. Among them, waste lithium ion batteries were taken as part of this responsibility.\textsuperscript{8}

According to the European Portable Battery Association (EPBA), the collected batteries are recycled to reuse and recover contained metals rather than to dispose them. However, batteries must be separated by their metal origins before the process can continue. For most lithium ion rechargeable batteries, they are processed to recover elements like cobalt, iron, and other metals.\textsuperscript{9}

Due to this document, Europe is leading the sustainable battery development and recovery industry over the US. The directive is part of the EU Sustainable Development Strategy to build a future without jeopardizing the ability of future generations to meet their own need.\textsuperscript{10}

The initiative is also utilized for energy storage with positive consequences across different fields. With energy efficient equipment that is a direct result of lithium ion recycling, portable appliances are more cost effective. This can be implemented in industries like the food industry. Machinery used for frozen foods packaging, farming/agriculture, and food processing for the supply chain of any major part of the food industry can have lower energy costs and emissions.

Ideally, the batteries of a given type will be standardized once the next best generation battery chemistry is established.\textsuperscript{7}

**China Initiatives**

In September 2015, China released regulations on Recycling of Motive Lithium Ion Batteries.\textsuperscript{11} It is the first explicit regulation to Li-ion batteries on how wasted batteries can be utilized. With this, Chinas lithium market can become the equivalent to Saudi Arubias oil market with its own control of the lithium production and manufacturing of the Li-battery. This is especially important to pay attention because most likely transportation will rely heavily on Li-ion batteries. Ziejian Li predicts the unique growth that China has over the industry especially in the electric vehicle business and eco-innovation in his study.\textsuperscript{12} By creating a system of production, consumption, and recycling, China can control the lithium ion battery market cycle in transportation.

**USA Initiatives**

Currently, the U.S. Environmental Protection Agency (EPA) does not regulate the disposal of batteries in small quantities. However, large quantities are regulated under...
the Universal rules of Hazardous Waste regulations (40 CFR PART 273). Lithium-ion batteries do not fall under it, and are not collected by manufacturers for recycling currently as well. As such, large quantities of lithium batteries are sent to the incinerator at a hazardous waste facility.\(^7\)

The US is attempting to put forth some type of regulation. The EPA is conducting a partnership with a screening-level life-cycle assessment (LCA) of currently manufactured lithium-ion (Li-ion) battery technologies for electric vehicles, and a next generation battery component (anode) that uses single-walled carbon nanotube (SWCNT) technology.\(^8\) Furthermore, other researchers are conducting research on recycling lithium batteries.

### Future Technology

As of 2015, some thoughts have been placed on the rechargeable nonaqueous lithium-air battery (Li-O\(_2\)). A group found that a reduced graphene oxide electrode, the additive LiI, and the solvent dimethoxyethane could reversibly form and remove crystalline particle (larger than 15 micrometers) during the discharge and charge cycle. The chemical nature has an impact on battery performance with an energy efficiency rate of 93.2% and 0.2 voltage gap. The technology has some promising results as the next generation energy storage, but the efficiency rate hasn't reached above 99.9% for a reliable long cycle life.\(^9\) As the shift from lithium-ion batteries happens, the initiatives in place for lithium can also apply to new technologies in energy storage that also rely on lithium. Lithium scarcity is possible and these initiatives lay the foundation for future policies should the need for it arises out of concern for health or limited lithium.

### Final Thoughts

Currently, there are a lot of buzzwords and promises in the media and Internet. There has not been an explicit regulation (besides China) imposed yet for Li-ion batteries simply because of the newness of the battery and market itself. The demand for the lithium ion battery will continue to grow.

With research ongoing, electric vehicles will rely heavily on Li-ion batteries unless another option is found. So, it is interesting to see what sort of regulation and policies will be implemented in the near future. There needs to be some sort of standard for these specific wasted batteries as this can impact cost, raw materials, emissions, energy storage, the grid of the future (smart grid), consumers, and maybe future industries. There may be materials and other development under wraps, but there is more information needed to expand on such an idea. The incentive is to have an innovative and adaptable battery for energy storage and to lower the overall cost of transportation, not create another scarcity issue. Recycling can be the answer to it.\(^10\)

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Combined Heat & Powers Role in Modern Grid System

Junyan Jiang
University of Illinois at Chicago, Chicago, IL

The 21st century needs a modern grid to meet increasingly higher standards in grid efficiency, reliability, security, power quality and environmental impact. Conventional coal-fired power plants, as the major electricity power house, are being phased out due to more stringent environmental regulations. However the electricity demand still persists. Combined heat and power (CHP) as a decentralized power generation system can support the transition and formation of the modern grid because of its high efficiency, enhanced system resiliency, improved power quality, reduced cost and carbon emissions, and its fast response complimentary to intermittent renewable energy. A case study was incorporated to demonstrate CHPs indispensable role in a modern grid configuration.

Introduction

Combined Heat & Power (CHP), also often called cogeneration, generates electricity and heat in an integrated system where thermal energy is captured and utilized for other applications. CHP is today the most efficient way of generating power. With more stringent environmental regulations to reduce carbon emissions as well as governments ambitious goal to install additional 40 GW CHP capacities by 2020, CHP as a reliable source of distributed power generation will be indispensable in a modern grid system. A modern grid refers to a reliable, resilient, secure, and environmentally responsible with consistent power quality and high efficiency grid system.

Status quo

As conventional coal-fired power plants are phasing out and the infrastructure of transmission and distribution is aging, the grid demands modernization. Based on the U.S. Energy Information Administration (EIA)s statistics, it is shown that the planned coal-fired power plant retirements continue to increase. (Figure 1) Given the need to comply with the Environmental Protection Agencies (EPA) Mercury and Air Toxics Standards (MATS) regulations, conventional coal-fired power plants are expected to be out of the picture. The continuous increase of natural gas-fired electricity generation owing to the low price caused by shale gas glut as well as the ever-increasing amount of renewable energy will help shape the future of the grid.

The transmission and distribution infrastructure needs upgrading as well. It is estimated that approximately 70% of transformers and transmission lines are over 25 years and more than 60% of distribution poles were installed 40 to 70 years, which are all approaching the end of their useful life.1

CHPs role in the transition & formation of modern grid

CHP as a form of decentralized power generation enjoys high efficiency, wide flexibility and reduced carbon emissions. CHP is a great alternative to avoid building large power plants. CHP systems can operate at the combined cycle efficiencies from a minimum of 55% to over 85%,3 whereas the electric generating efficiency of a conventional power plant is around 36% since the thermal energy is completely wasted. CHP can provide a wide range of capacity from one kilowatt to hundreds of megawatts in various applications including industrial manufacturers, institutions, commercial buildings, and municipal and residential developments. CHP can adopt different fuel sources not limited to natural gas, biomass, biogas or a combination of previous three. CHP can reduce the carbon emissions by almost half of the conventional generation. (Figure 2)

A strategically well-sited CHP plant can improve system resilience and power quality. CHP largely powered by natural gas can generate electricity independently off the grid in the case of catastrophes or power outages caused by grid failures. Furthermore the U.S. Energy Information Administration (EIA) estimates that electricity transmission and distribution averagely losses about 6% of the electricity that is transmitted and distributed annually in the United States.4 Having an on-site CHP

![FIG. 1: Scheduled 2015 capacity additions mostly wind and natural gas; retire mostly coal. Taken from 2.](image-url)
plant can significantly avert or mitigate the transmission and distribution power line losses especially during the peak load when the utility power line losses increase exponentially.

CHP can receive its permit and be built much faster than large power plants. A major centralized power plant and transmission line usually undergo a long process of decision-making, land acquisition, design and contracting before being built. A large power plant is also usually constrained in site selection as it requires a large amount of water to cool the system. Unlike large power plants, CHP is not limited to its location. In this regard, CHP can reduce the investment risk and expedite the development schedule substantially.

CHPs fast response can address the intermittent issue of renewable energy like wind and solar. CHP can ramp up and down rapidly. This feature can be utilized to generate electricity when wind and solar resources are not available. Such application can be very practical in a microgrid deployment. (Microgrids are modern, localized and small-scale grids compared to the conventional grid with centralized power generation.) Microgrids can connect and disconnect from the centralized grid and operate autonomously which can improve the grid safety and reliability tremendously. A case study will be demonstrated about the function of CHP in a form of the modern grid - microgrid.

Moreover from an economic perspective for utility companies, a well-located decentralized CHP plant can prevent or at least reduce transmission and distribution investment. A conventional centralized power plant requires building new and/or upgrading existing transmission and distribution system. Also for individual facilities, owning a CHP can alleviate the peak load which in return will save marginal utility cost and demand charge.

CHP is still faced with a few challenges - unfavorable policies for utilities and high capital cost for individual facilities. Favorable policy, incentives, subsidies and reciprocal business models become crucial in promoting CHP in the modern grid system to realize a win-win scenario for CHP customers, utility companies and ratepayers.

Although every state’s policy differs, we divide the electric markets into two categories - regulated and deregulated. For the regulated market, utility companies generally can integrate CHP in their rate base and are fully allowed to enjoy the high efficiency of CHPs although they may have to account for all the risks. On the other hand in the deregulated market, electric distribution utilities cannot own power generation assets, which poses a barrier that prevents utilities from fully utilizing CHP plants.

In most deregulated markets distribution utilities have contracts with third party CHP owners and only run CHPs during peak load as a contingency plan whereas utilities cannot fully benefit from CHPs high efficiency and third parties do not get high standby rates. If the policymakers can take all the CHP’s benefits including high energy efficiency, environmental endeavor, and diminished transmission and distribution costs into consideration and promulgate favorable policies for larger deployment of CHP, all the parties involved can truly benefit from CHP.

For individual facilities, it is understandable that business owners are apprehensive about investing high capital cost in energy generation equipment rather than the core business they are familiar with. However ancillary services to sell excessive electricity and opportunities to sell surplus thermal energy to neighboring facilities could be very persuasive for individual facilities to own CHP plants. For example Princeton University gets paid back for its CHP electricity generation at about $600,000 per MW annually for its participation in PJM’s ancillary services market. And the Great River Energy Spiritwood Station in Jamestown, ND CHP project successfully supplies steam to Cargill Malt plant and the Dakota Spirit AgEnergy biorefinery maximizing the overall efficiency to offset the operational cost.

An even better business model for individual facilities is having electric and/or natural gas utility companies make the initial capital investment and charge the consumer a fee each month. An example is University of Wisconsin, Madison West Campus Cogeneration Facility, a 150 MW natural gas-fired facility which provides the electricity to Madison Gas and Electric (MGE) customers and steam and chilled water to the UW-Madison campus. MGE owns the electric production part of assets while UW-Madison owns the steam heat and chilled-water assets. Such agreement was reached so that the campus, utility and ratepayers could all enjoy the high efficiency and economy of CHP.

FIG. 2: Combined heat and power configurations. Adapted from 3.
A case study of CHPs role in Princeton University - Microgrid

Princeton University's Microgrid configuration is composed of a CHP plant with a gas-turbine power generator, solar panel field, thermal storage (chill water), delivery network and smart control. (Figure 3) The CHP plant was constructed in 1996 which replaced the old coal-fired boilers and was awarded the Energy Star CHP Award in the following year. It is capable of producing electricity up to 15 megawatts and steam which is used for heat, hot water, sterilization, heating and cooling for roughly 180 campus buildings. Its overall efficiency is around 75% to 85%.

Most electricity on the campus is generated by the CHP plant. The solar panel field contributes 5.5% of total power generation. The chilled water energy storage gives the option to offset the peak load by making chilled water at night and consuming it during the day.

According to EPA, Princeton University's CHP system requires 20% less fuel than typical purchased electricity and onsite thermal generation, reducing carbon emissions by an estimated 28,000 tons annually.

An advanced real-time dispatch system as a means of smart control is utilized to determine the most cost effective way for Princeton University to supply electricity whether to generate it onsite or purchase it from the utility company. When campus demand is high and power is expensive, the campus generates the electricity itself and when at night the demand is low and electricity is cheaper to purchase than generate, the campus draws more power from the utility grid.

Princeton University participated in PJM's ancillary services market in New Jersey's deregulated market in 2013. The system became dispatchable directly by PJM but campus operators can still override at any time. The campus can sell electricity back to the grid.

In the event of Hurricane Sandy struck New Jersey, the Princeton area was blacked out for two days. However with the microgrid configuration, Princeton University was able to go off grid and served as a safe harbor for many. The CHP generated 13 megawatts and powered the campus until the grid went back on. After all, the heart of the Princeton microgrid configuration is the CHP plant.

It is the CHP plant that enables the campus to enjoy high efficiency, decrease carbon emissions, incorporate intermittent renewable energy use, improve grid resilience, and optimize operational cost.

Conclusion

The 21st century needs a modern grid. A modern grid will be more reliable, secure, economical, efficient, and environmentally friendly so that it can continuously serve as the backbone of our national economy. With the globally enforced mitigation of climate change, large scale coal-fired power plants will eventually be superseded.

CHP as a decentralized power generation means has gained more and more recognition of its great value. The dCHPP (CHP Policies and incentives database) provided by EPA is an online database to search for CHP policies and incentives by state or at federal level. It is a government initiative to promote CHP. CHP with numerous benefits plays a critical role in the transition and formation of the modern grid system. It can improve the overall efficiency, reduce carbon emissions and strengthen the reliability and resilience of the modern grid.

CHP as distributed power generation can synergize the formation of microgrid, a modern, independent yet interconnected grid system. It can leverage the modern grid to incorporate more renewable energy and energy storage. CHP will ultimately underpin the modern grid.

4 United States Energy Information Administration, Frequently asked questions - how much electricity is lost in transmission and distribution in the united states (2015), URL http://www.eia.gov/tools/faqs/faq.cfm?id=105&t=


Flow Batteries Storing Energy on the Grid

Vineeth Kumar Gattu  
University of Illinois at Chicago, Chicago, IL

The demand for electricity produced from renewable sources, such as wind and solar has considerably increased in the past decade, largely owing to the need for clean energy with no environmental impact and carbon sequestration. The energy generated from intermittent sources: wind and solar is dependent upon various climatic and geographical conditions, serves as the driving force for storing energy on grid in suitable energy packing systems to be utilized at peak hours. Consequently, the capacity to store vast amounts of energy is rising. Flow batteries have gained significant importance during the recent years owing to the performance and ability to store vast amounts of energy. This paper reviews popular types of flow batteries, current trends, and future measures to optimize the performance for long-term durability of these flow based energy storage devices.

Introduction and Overview

The technology for intelligent grid operations and storage of excess and intermittent energy produced from renewables is ripe for transformation. A fifty-year period has witnessed transitions in technology in the past; currently the world is heading towards a major revolution, whereas harnessing sustainable clean energy sources, such as wind, solar and issues related to carbon sequestration, global warming, and climatic changes are a top priority.

As the world looks towards more clean energy technologies, renewable sources are of great importance to reduce the detrimental environmental impact by the conventional fossil fuels. The U.S. Energy Information Administration (EIA) estimates today (2014) about 11% of the worlds marketed energy consumed originates from renewable energy sources, such as biogas, geothermal, solar, wind, and hydropower with expected increases of approximately 15% by 2040. In addition, the EIA also estimates about 21% of electricity produced was possibly from renewables and will likely increase to 25% in 2040. The gap between energy produced and consumed from variable sources on grid is high and utilization of renewable energy sources to the maximum possible extent is highly encouraged. Hence, the motivation towards storing excess energy in various storage systems is of high interest.

Issues, such as renewable energy penetration, resource scarcity, grid stability, and changing regulatory formula have driven the search for alternative sources of energy storage. Consequently, as the technology advances, the slice of electricity produced and consumed from renewables is increasing and electricity produced from these sources being intermittent. It is of growing importance to store the vast amount of clean energy on the grid in suitable energy package systems.

Energy Storage Options

Fundamentally, the drive is to store excess energy generated during off-peak hours or from variable sources in any physical form to be-used during demand periods. Forms of energy, such as potential, kinetic, electricity, and chemical are available, whereas the advanced technology to exploit these energy storage forms necessitates consideration. Energy storage is defined by a specific requirement, such as storage for electricity, grid energy storage, renewable storage systems, and energy storage in chemical fluids also needs attention fluids; also requiring attention based on requirements and energy storage methods that methods that have been developed.

Figure 2 shows various energy storage options available. The plot reports discharged times (at rated power) compared to the energy storage size, while Pumped Hydro and Compressed Air and Energy Storage (CAES) show very high discharge times with capacity followed by electrochemical storage systems such as flow batteries, Advanced lead-acid battery show a great potential to serve as back up for the grid power once the capacity could be increased to GW scale storage with research and technological advancements.

FIG. 1: Energy Consumption in the United States, March 2015.
Storing Energy on Grid

One of the main concerns of the 21st century is the transformation of the grid to integrate the renewable energy sources. However, advancement of energy storage technologies could possibly avoid the transformation largely and investing in potential technologies for grid energy storage could be more sustainable. Storage technologies could address issues, such as operating capabilities, lowering costs, and high reliability which points to a robust grid and resilient electricity delivery along with the emergency preparedness.

Figure 3 shows the status of the U.S. or grid energy storage. Reported as of August 2013, 202 energy storage systems were installed for the grid. Further, this illustrates 95% (23.4 GW) a major portion of energy on the grid is stored in pumped-hydro and the remaining 5% (1.2 GW) in the form of batteries, thermal energy storage, compressed air systems, and flywheels. The pumped-hydro storage technology is fully mature and currently used at various sites around the United States. However, this technology is very specific to the geographical location, such as mountains and hilly areas; making pumped-hydro a site-specific storage system. Such is the case with the CEAS, the geographical location matters yet the two storage systems have the potential to enhance the stability of the grid while integrating the intermittent renewable sources.

Figure 4 shows the various energy storage technologies and current stage of maturity. Again, information indicates that Pumped Hydro is quite developed and owing to its limitations, the search for alternatives, such as electrochemical capacitors, flow batteries, and magnetic energy storage systems under demonstration stage are future potential storage technologies.

Electrochemical storage and flywheels currently deployed in demonstration scale are site-independent and targeted for short discharge times about few seconds to about six hours of backup power. Technological advancement in battery technology cutting down material costs will play a major role in harnessing the latent storage potential along with many other benefits, such as being robust and scalable to the requirement of grid operations.

Electrochemical Storage Systems

Systems based on principles of electrochemistry discovered in the late 1700s, about 200 years old now and technology has a high potential for energy storage on grid and for transportation owing to discharge times close to existing requirements of the grids. However, the grid storage capacity is the main concern to address. Electrochemical storage devices, such as batteries and super capacitors play a major role in SLI (starting, lighting, and ignition) of many devices and vehicles from cars, aircraft, toys, and cordless tools to satellites, pacemakers, and computers.

Electrochemical processes involve the electron transfer across a potentially different barrier based on Faradays laws and this generates electricity. The chemical reactions take place in an electrochemical cell shown in Figure 5, commonly known as redox reactions. The cell package contains two electrodes: an anode (loses an e-) and a cathode (gains an e-) along with electro-active species known as an electrolyte. Electrolyte is a medium via electron transfer occurring during the chemical reaction and a change in the oxidation state of the two electrodes.

Electrochemical means of storing energy is customizable to the specific requirements or simply based on the duration of storage. For long-term options, storing
high-energy contents outside the cell is ideal in a least expensive and efficient manner; contents will be transferred when energy is needed. In addition, this ensures a long-life of the expensive parts of the cell package which otherwise could be eroded due to active species present in the electrolyte. Considering short-term storage, the rechargeable batteries play a crucial role in many devices, such as mobile phones and laptops. These batteries are expected to deliver power anywhere between a few hours to weeks. In addition, these batteries need replacement more frequently than the corresponding long-term storage considering all the contents are part of the cell package.

**Flow Batteries for Grid-Energy Storage**

Flow-based electrochemical energy storage systems have many advantages over the solid-state rechargeable batteries. The electroactive species involved in the electron transfer is outside the cell and makes the battery capacity independent of quantity present in the cell package unlike solid-state rechargeable batteries. In addition, the electroactive species outside the cell not only increase the life of the battery, but allow the flow battery capacity to be scaled up independently; this addresses the GW-scale energy storage required for grid power back-up. This drives the importance in flow batteries to be a better solution for long-term energy storage concerning grid energy storage, this is most likely the best means of storing the intermittent energy from renewables.

Flow battery is a type of rechargeable battery where electricity is generated by the ion exchange process between two electrolytes. The electrochemically active components in the electrolytes circulate against each other to generate a charge and are charge separated by a thin membrane and surrounded by a positive and negative electrode. The construction principle of a flow battery is based on directly converting chemical energy to electricity directly. Flow batteries developed based on this requirement are redox, hybrid, membrane less, semisolid, organic, metal hydride, and nano-network.

**Flow Batteries - Vanadium Redox Couple**

The Redox flow battery (RFB) is a type of rechargeable flow battery based on the principle of chemical reduction and oxidation in the package to store energy in liquid electrolyte solutions, which flow through negative and positive electrodes. Most popular and extensively studied redox flow batteries are Vanadium Redox Flow Batteries (VRFB). Figure 7 displays a schematic of the Vanadium redox battery, clearly showing the cell package independent of the electrolyte containing tanks. A positive electrode side tank contains the oxidized Vanadium ions (V5+/V4+) and the negative electrode side contains the reduced Vanadium ions (V3+/V2+). A number of cells are stacked together in a series to produce a battery, which can store and deliver kW-scale energy.

Vanadium has the ability to exist in different oxidation states (V+2, V+3, V+4 and V+5) in the solution and, this property makes battery use only one electrochemically active species instead of two. The liquid electrolyte is the most important part of the Vanadium RFB since contents of the cell package are stored, and the performance of the flow battery is dependent on the concentration of the electro-active species in the electrolyte within temperature range stability required for the operation of the electrolyte.

Vanadium-redox batteries are the most commercially advanced flow batteries available and now in development; yet their use is limited by the stability of $V^{+5}$ cation in a narrow temperature range ($10^6$C to $40^6$C) and low energy density ($< 1.7M$) vanadium species concentration. The precipitation of $V_2O_5$ powder dur-
FIG. 7: Schematic of Vanadium Redox (VRB) Flow Battery system.\textsuperscript{9}

ing battery operation leads to clogging of the battery. However, the research carried out under the Joint Center for Energy Storage Research (JCESR) is addressing these issues with VRFBs.

Generally, the VRBs have an open circuit voltage of 1.4V, however, the D.C. performance characteristics depend upon the size and number of cells. In addition, no issues exist regarding self-discharge since the electrolyte is stored out of the cell package. The life of a VRB system is mainly assessed by calculating the life cycle of the components of the cell package, which is approximately 10 years. The pumps, tanks, and other electronics usually have a longer life along with the electrolyte materials, which do not degrade over time.

Concerning the response to the grid; VRBs have zero to full output within milliseconds and for a shorter duration of power, the electrolyte within the cell package may be sufficient without utilizing electrolyte contained in tanks.\textsuperscript{12}

Organic-Inorganic Flow Batteries

The Vanadium RFBs are currently used on small-scale storage applications; their deployment on a large-scale is hindered by the insignificant availability and cost of precious materials involved is once again high. In 2013, researchers at Harvard demonstrated a metal-free organic-inorganic flow battery. Unlike conventional RFBs, this battery is based on the aqueous redox chemistry of small organic molecules called Quinones. The redox active materials containing no metals can drastically reduce materials cost, in this aspect the most important being the electro-active species. The battery has demonstrated performance similar to the VRBs. The metal-free battery uses a member of earlier stated Quinone family; 9,10 anthraquinone-2,7-disulphonic acid (AQDS) as the charge carrier and the different Quinone structures are shown in Figure 8.

The cell schematic is shown in Figure 9 is in the discharge mode, the solution AQDS is pumped through the negative electrode in sulphuric acid and the Br\textsubscript{2} gas is pumped in HBr which is a positive electrode side of the flow system. Carbon electrode acts as both anode and cathode. Researchers reported use of a theoretical approach to understand the $E^0$ of the Quinone/Hydroquinone couple. Electrochemical studies show that AQDS molecules undergo fast and reversible two-electron two-proton reduction on inexpensive carbon electrodes without the addition of electrocatalyst. An aqueous flow battery involving the Quinone/Hydroquinone couple has achieved a peak power density exceeding 0.6 W/cm\textsuperscript{2} and has undergone over 700 deep discharge cycles with over 99.9% capacity retention per cycle.

Conclusions

1. Integrating renewables primarily wind, solar, and improving the existing grid transmission, is the impending energy scenario for the next fifty years. Demand for clean energy to reduce climate changes and carbon sequestration is expanding to increase efficient energy produced from intermittent sources.

2. Concerning energy storage, apart from integrate renewables; this has many other benefits such as
managing peak load, grid stabilization, reliability, resiliency, and emergency preparedness. In addition, this gains importance when the demand exceeds production during peak hours of the day and storage could provide a foundation the electricity pricing being more stable.

3. Energy storage methods are extensively studied across the world. Currently, pump-hydro dominates with around 95% storage. However, being site-dependent creates unreliability for grid storage. Electrochemical methods for grid energy storage have gained sight in the past decade, and this field awaits a major transformation to answer delete growing demands for shifting away from fossil fuels towards renewables.

4. Flow batteries could possibly answer the future of energy storage since solid electrode batteries are drained very soon when discharged from full power. In the near future, flow batteries will be favored in the near future for their ability to store large amounts of energy on the grid clean, cheap, and efficient manner. For their capacity to cleanly, cheaply, and efficiently store vast amounts of energy on the grid.

5. Currently, the battery industry is possibly shifting away from the traditional metal-based batteries. The absence of the active metal components and readily available earth-abundant organic molecules known as Quinones will drastically reduce the cost of grid electricity energy storage.

What is CHP?

Combined Heat and Power (CHP) is an efficient way to generate electricity and heat by utilizing the waste heat from the electric generator in place of heat from a separate boiler. Currently, most electricity is purchased from a central utility company that generates power at 35% efficiency; the balance of fuel input energy is lost as heat. With CHP some of the electricity is generated onsite and the waste heat from the generator (water jacket and exhaust) is used for space and water heating and other industrial processes that require heat. This reduces the fuel requirements to the boiler which also reduces emissions of Green House Gases (GHG) and other pollutants. Overall CHP efficiencies can make upwards to 85%. CHP is also known as Buildings Cooling, Heating & Power (BCHP), CHP for buildings (CHPB), Integrated Energy Systems (IES), Total Energy System (TES), Tri-generation (Trig-en) and Cogeneration.1 CHP is best fit where there is demand for heat (or cooling load) and electricity is simultaneous e.g. hospitals, the hotel industry, educational institutes. Exhaust heat can be applied to support cooling loads with absorption chillers.

CHP position in current energy market

There are more than 4,100 CHP sites in the USA with 81,800 MW installed capacity. As per ICF International there is 65 GW of industrial technical potential for CHP systems based on thermal demand of the site which does not include the potential for producing electricity for export to the grid beyond the site/facility’s demand. There is 130 GW of potential for CHP systems based on thermal demand of the site with exporting the over produced electricity to the grid or sold to adjacent users.2 A country like Denmark uses district heating & CHP to drive towards efficiency and energy self-sufficiency. Over 50% of power is generated by CHP systems in Denmark vs 8% to 9% power generated by CHP in the United States, considering the total power generation in the USA is way bigger than Denmark.

CHP Systems

There are different types of fuels and prime movers used to run the CHP system. Natural Gas, Propane, Methane, Oil, Coal, Landfill Gas, Digester Gas, and Hydrogen are commonly used fuels. The role of the prime mover is to convert fuel energy directly to mechanical energy, shaft power. The mechanical energy can then drive a generator to produce utility grade electricity technologies used for generating electricity on-site or near the site. There are many proven prime movers. Reciprocating Engines, Gas Turbines, Microturbines, and Steam Turbines are commonly used prime movers.3

Energy reliability

CHP offers a variety of commercial, environmental and societal benefits; including grid reliability and energy efficiency. CHP can significantly reduce emission of carbon dioxide and air pollutants like nitrogen oxide, sulfur dioxide and volatile organic particles. CHP facilities are located on-site or close to consumers so electricity transmission and distribution losses are reduced and delivery reliability is enhanced. Compared with large, interconnected grids, CHP is more resilient when weather or security events interrupt energy supplies. CHP can be integrated with microgrids for grid reliability and resiliency. Many facilities can come online quickly after outages and can operate off the grid during a blackout. These CHP features allow businesses to keep going and to maintain critical infrastructure powered.4,5

CHP present Challenges

Financial

Because CHP equipment has significant upfront costs and it’s a long-term financial commitment, CHP is a
Most environmental regulations for power generators and boilers have established emissions limits based on heat input or exhaust concentration: that’s how emission is measured in pounds per million British thermal units (lb/MMBtu) of heat input or in parts per million (ppm) of pollutants in the exhaust stream. These traditional input-based limits do not account for the pollution prevention benefits of process efficiency in ways that encourage reduced energy use. Output based environment regulations (OBR) encourage energy efficiency and clean energy supply. OBR have been used for years in regulating some industrial process. OBR encourage energy efficiency and clean energy supply. CHP units produce both electrical and thermal energy output. OBR can be designed for both types of output in compliance computation. Thermal output is very important because CHP achieves its best energy efficiency by generating both electrical & thermal energy from a single fuel source. Although CHP has many environmental benefits, there are very few incentive programs or policies to support it like other renewable energy programs.

**What’s next to overcome challenges?**

**Third Party ownership structure**

In deregulated states, electric utilities cannot own electric generation directly, but there are some models that allow them to employ CHP. A United Illuminating company in Connecticut developed a zero-capital program where the third party owner works with customer interested in having CHP on-site. Five to ten year contracts are encouraged between the third party (CHP Owner) and customer. An electric and natural gas utility (at this stage decided to be unnamed) developing a model where CHP Initial capital investment will be made by a financial institution or investor but the CHP system will be sited at the customer’s facility. The customer gets the direct benefits of the electricity and heat generated from CHP system. The customer will pay a flat fixed rate each month for ten or fifteen years as per contract and after that customer will be allowed using electricity and thermal energy produced on-site for no additional cost. The customer will enjoy a lower monthly payment operating budget than capital investment and the investor will enjoy a fixed monthly payment that offers a rate of return on its investment.

Fig 2 shows the flow of money and electricity provider and user. Per contract CHP owner gets money from the customer and utility, the customer gets electricity and heat from CHP system, and utility receives over produced electricity from the customer. Utility does not have to make any initial investment to update the grid to meet the customer increased demand. CHP owner owns the
system based on contract terms and conditions. It is win-win situation for utility, CHP owner and the customer.

In Regulated states, electric utilities own CHP or enter in PPAs (Power Purchase Agreements) for power produced by CHP. CHP cost is aggregated with other costs and embedded in the utility’s rate base. In Alabama Power territory, Southern Company owns over 700 MW of CHP across six plants in which the utility, customers and rate paying customers enjoy benefits of CHP.

**CO₂ emission saving calculation**

EPA and state air regulatory authorities have supported CHP deployment due to significant reduction in harmful emissions. CHP projects need to quantify the fuel and carbon dioxide emission savings compared to conventional separate heat and power (SHP).

To calculate the fuel and CO₂ emission saving for the CHP system, thermal and electricity output should be calculated separately for heat & power. Table I show a summary of a CHP emission calculator based on 10 MW natural gas-fired combustion turbine and heat recovery with default values in the calculator at the facility (e.g. Hospital, College campus) in Illinois state. Operation hours 7500 per year and the fuel heat rate 11,728 HHV have been assumed for input values. In this example output heat has not been utilized for absorption chiller but CHP system can be designed to utilize the heat for absorption chiller.

**Emission Reduction due to CHP system**

Figure 4 shows the output results of the calculation based on Table I inputs. 10 MW CHP systems can reduce the 67,581 tons of carbon dioxide equivalent, which is equivalent to approx. 12,814 passenger vehicles. Depending on the geographical location, CO₂ emission calculation is an important factor to show the CHP environment benefits. EPA has updated the CO₂ emission calculator in January 2015.

A number of federal, regional, and state programs have adopted output based emission regulations. EPA used output based emission regulation (OBR) approach to revise the electric utility boiler New Source Performance Standards (NSPS). This action reflected a major change for NSPS and provided an efficiency based rationale for transitioning to output based regulation. OBR approach is very important for CHP systems. CHP & EPA Partnership (CHPP) developed a handbook to assist state, local, and tribal regulators to develop output based regulations. The handbook provides practical information to help regulators decide if they want to use output-based regulations and explains how to develop an output-based emission standard.

**Clean Air Act Section 111**

EPA has released the final version of the Clean Power Plan, a rule that sets performance rates and individual state targets for CO₂ emission from an existing power plant on August 3, 2015. Under the Clean Air Act emission reduction is set for 32% nationwide by 2030 respect to 2005 level. CHP can help states to meet their Clean

TABLE I: Important parameter for the CHP emission calculator based on 10 MW natural gas-fired combustion turbine and heat recovery system.

<table>
<thead>
<tr>
<th>CHP Technology</th>
<th>Combustion Turbine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
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<td>Number of Units</td>
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<tr>
<td>Total CHP capacity</td>
<td>10,000 kW</td>
</tr>
<tr>
<td>Operation</td>
<td>7,500 year BTU/kWh</td>
</tr>
<tr>
<td>Heat Rate</td>
<td>11,728 HHV</td>
</tr>
<tr>
<td>CHP Fuel Consumption</td>
<td>879.633 MMBTU/year</td>
</tr>
<tr>
<td>Duct Burner Fuel Consumption</td>
<td>Total Fuel Consumption</td>
</tr>
<tr>
<td>CHP Fuel Consumption</td>
<td>879.633 MMBTU/year</td>
</tr>
<tr>
<td>Duct Burner Fuel Consumption</td>
<td>0 MMBTU/year for electrical applications (cooling and electrical heating)</td>
</tr>
<tr>
<td>Total Fuel Consumption</td>
<td>879.633 MMBTU/year</td>
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<tr>
<td>Total CHP Generation</td>
<td>77,000 MWh/year</td>
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<tr>
<td>Useful CHP Thermal Output</td>
<td>390,870 MMBTU/year for thermal applications (non-cooling)</td>
</tr>
<tr>
<td>Total</td>
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</tr>
</tbody>
</table>

FIG. 3: Calculated emissions for conventional and CHP energy production.
FIG. 4: Reduction in emission due to CHP project, which is the equivalent of 67,581 tons of CO₂.²

Power Plan targets. ACEEE develops the CHP template to help states to understand how to document and claim emission reduction by CHP. ICF International estimates an additional 40 GW of CHP would reduce about 150 million metric tons CO₂ annually, which is equivalent to the emissions of over 25 million cars.

Under Clean Air Act section 111d plan, states have engaged in a variety of policies and programs to support CHP. Here are the examples:

1. Interconnection standards and procedures: Statewide technical standards and streamlined procedure for connecting CHP to transmission and distribution network.
2. Energy saving target: Allowing CHP to qualify in state energy saving standards.
3. Financial assistance: Incentives, grants and eliminate loan programs, barriers to CHP deployment.
4. Streamlined permitting: Output-based emissions regulations (OBR) & “fast-track” air permitting for qualified systems encourage CHP deployment. Shorter time for permitting can make a significant impact on CHP deployment and financial saving. For example, one “fast-track” air permit for CHP in Texas reduced well over 1 year time to acquire the state level air permit to 4-6 weeks. Such short permitting time saves lot money on CHP projects. EPA has developed a handbook for output based emission guideline.

Conclusion

CHP is a proven solution for meeting growing energy demand efficiently, cleanly and economically. CHP is a clean energy solution that immediately addresses a number of national priorities, including improving the competitiveness of U.S. manufacturing, increasing energy efficiency, reducing emissions, enhancing our energy infrastructure, and improving energy security. CHP has its own challenges, but the future is good with new Clean Air Act section 111 & third party investment structure. The Obama Administration is supporting a national goal of achieving 40 GW of new cost effective CHP in the United States by the end of 2020. To meet this goal by 2020 barriers to CHP development needs to be removed, and effective policies, programs and financing opportunities promoted.

1 Midwest CHP Application Center, *Chp resource guide (second edition).*
4 Chp systems.
6 Center for Climate and Energy Solutions, *Cogeneration / combined heat and power (chp),* URL http://www.c2es.org/technology/factsheet/CogenerationCHP.
Short Term Energy Storage on Grid

Selamhan E. Kazokoglu  
University of Illinois at Chicago, Chicago, IL

This paper summarizes short term storage applications for electric grid that are available today. It focuses on U.S. Electric grid and current challenges of interconnected electrical generation and distribution. Differences between short term and long term energy storage systems are explained with more detail on short term technologies, current and the possible applications on electric grid. For comparison purposes rated power discharge times, reaction times, life cycles as well as per unit power and per unit energy costs are presented.

Introduction

U.S. Electric Grid Today

Current electric transmission and distribution infrastructure in the U.S. is a large system that involves 170,000 miles of high-voltage cables, 6 million miles of low voltage transmission cables, substations, distribution centers, 19,243 generators of at least 1MW installed at 7,304 power plants as of April, 2015. This system serves more than 143 million customers in U.S.1,2

The grid system in the U.S. is divided into three independently synchronized areas or interconnections; Eastern Interconnection, Western Interconnection and the Electric Reliability Council of Texas.3 These divisions are mainly due to the challenge of synchronizing large grids and keeping them separate results in a more reliable system. While there are no AC connections between these three systems, there are high-voltage DC lines. In case of a major system failure in any of the interconnections, the other will not be affected, but during normal operation these connections allow energy exchange as if they are one big system coast to coast.

Challenges of the Grid System

Several challenges emerge with a system of this size and complexity. Keeping the system running can be difficult when unexpected events happen. The goal is to carry electric energy from power plants to end customers, commercial, residential or industrial. However, unexpected events may happen, such as storms, transmission equipment failure, transmission line interruption, unplanned shutdown of generation, physical or cyber-attacks. Under any circumstance the grid should be secure and ready to provide reliable, stable power to end users.

Additionally, renewable sources while providing clean energy from sources like sun and wind have fluctuating weather dependent outputs. Suppressing fluctuations in frequency and voltage in renewable sources is mandatory in order to safely feed renewable energy to grid. Another issue with renewable generation is variability. Wind power, for example, tends to peak at night when demand decreases to a point where generated electric energy has no place to be used.

Nuclear power plants traditionally are run continuously regardless of the demand on the grid. This is due their high construction and high operational costs, and the difficulty and risks of adjusting nuclear reaction rates in their core, which control power generation rates. While newer plants can be adjusted to a certain level, which is called load following, in general nuclear plants also feed the grid with unnecessary energy during off peak hours just like wind farms.

Energy Storage Systems

Electric Energy Storage

Storage systems provide reliable, secure and redundant operation of the grid. Storage technologies help renewable sources to integrate into the current grid system. They provide grid scale back-up power which can be utilized during peak or emergency demand. By storing power during periods of low demand and releasing it during periods of high demand they defer investments in more generation capacity. Similarly, electricity can be stored at the origin and termination of transmission lines, allowing plants to operate at their most efficient current levels continuously, independent of supply and demand cycles. It is no surprise grid scale storage systems are used all over the world. Electric storage on U.S. grids, as of August 2013 was 24.6GW and a major portion of this storage, nearly 95%, is pumped hydro plants.3 However 21.6 GW of hydro storage is only a fraction of 2014 U.S. total electric production of 4,092,935 GW.4

Classifying Storage Methods

Storing electricity presents a severe technical challenge: it cannot be captured or stored and held stationary for later release. Instead, electric energy must to be converted to another form of energy which can be stored and converted back to electricity on demand when needed. This conversion technique is one way to classify a stor-
Electricity can be converted to mechanical, electrochemical, electric or magnetic field storage. Mechanical storage systems convert electrical energy into kinetic or potential energy. Using electricity to spin a rotating mass to several thousand revolutions per minute as in flywheels is converting to kinetic energy, and pumping water up to a higher elevation, as in pumped hydro, is converting it to potential energy. Another example of potential energy conversion would be CAES, compressed air energy storage, where air is compressed into an underground cave to be released the next day to operate a turbine during high demand.

Electrochemical storage is uses electric energy to drive a chemical reaction either in a rechargeable battery or generating hydrogen for later use in a fuel cell or gas turbine. Rechargeable batteries are a very broad subject alone and will be discussed only as a method of storage but different chemistries will not be compared individually. Produced hydrogen can be utilized two ways; it can be fed into natural gas lines up to 15% without requiring significant changes to end-user appliances or pipelines and used when it is needed. It can be used in a furnace or generator turbine, both methods capture excess electricity a chemical method.

Field storage can be electrical or magnetic. An electrical field is produced when two conducting plates come close and an electric potential is applied. This setup is a simple capacitor. With several advancements in materials, certain capacitors are now called super- or ultracapacitors. Capacitors store electric energy in the electric field they create. Energy can also be stored in a magnetic field created by electrical currents circulating in a solenoid. The most efficient magnetic field storage systems use superconducting solenoids, as in superconducting magnetic energy storage.

Storage systems can also be classified by time of discharge and response. Discharge time shows how long a storage system can supply its rated power. Response time shows how fast it can change its power output. For instance a pumped hydro plant, depending on its reservoir, may have a long discharge time, anywhere from hours to days. However, it will not respond to a voltage drop in 10-20 milliseconds. For an application where milliseconds count, a flywheel, super-capacitor or battery systems will be required since even spinning reserves will take several minutes to ramp-up.

**Short Term Storage Systems**

**Defining Short Term**

Issues such as transmission equipment failure, line interruption, unplanned shutdown of generation, time shifting electrical energy due to economic reasons are being solved by long term storage techniques such as batteries, pumped-hydro or hydrogen generation. An example is a wind farm powering a hydrogen generator during off-peak hours of the day and pumping this hydrogen to a peaking gas plant to meet high demand during the next day. Pumped-hydro is similar, excess energy on the grid is used to pump water from a lower reservoir up to a higher reservoir during off peak hours such as nights and weekends, then letting this water flow down thru generators during the day when there is additional demand. Upper basins could be anywhere from 30m to more than 800m higher than the lower water reservoir. Compressed air systems and batteries work on the same principle, storing electricity when it is inexpensive and abundant, putting it back on the grid when it is needed or more profitable.

Short term storage systems can respond very fast, ramping up or down in milliseconds when there is a need on the grid and quickly ramping back. They discharge fast and they are able to cycle frequently from full charge to empty. Short term storage technologies are used for grid stability, reliability and power quality applications. These applications require voltage regulation, frequency regulation and angular stabilization. As stated above, discharge capability in milliseconds is very important; fluctuation suppressions, frequency excursions, voltage or angular stability corrections should be addressed in less than 1/3 cycles. Therefore storage systems for those applications must be capable of responding on these short time schedules, and be ready at all times.

**Types of Short Term Storage**

**Supercapacitors** Capacitors store electrical energy by creating an electrical field on two conducting plates which is separated by a non-conducting material called dielectric. Applying a voltage difference to the plates will charge the capacitor. This charge can be utilized by connecting the plates to an external load which allows the electrons to flow as the capacity will discharge. Capacitors that have orders of magnitudes of higher energy densities are called supercapacitor. The increase in energy density is achieved by increasing surface area of the plates since amount of charge a capacitor can hold is directly related to this area. In order to increase the plate area highly porous materials are used such as activated carbon which achieves areas of more than 2500 m² per gram. Plate separation is less than 1 nm, which requires a liquid dielectric. This dielectric can be either aqueous or non-aqueous. The disadvantage of this design is the required electrolyte, the liquid dielectric, cannot withstand higher voltages hence limiting supercapacitor voltages to 3 V per cell for organic, non-aqueous or 1V per cell for aqueous acid based electrolytes. Charging supercapacitors beyond these voltages will degrade the electrolyte causing internal short circuits. For practical uses supercapacitor need to be serially connected in order to increase voltage.
Superconducting Magnetic Energy Storage - SMES

Superconducting magnetic energy storage systems (SMES) create a magnetic field on a cryogenically cooled superconductor coil. System is maintained at as low as 1.8 K using liquid helium or liquid nitrogen.5-8 A SMES consist of three main parts; (1) Power conditioning system, (2) Superconducting coil, (3) Cooling system. SMES systems have more than 20 years design lifetimes during which performance loss is insignificant. The advantage of energy stored in magnetic field is the ability to discharge in less than 0.5 milliseconds.11 SMES can charge again as fast as it can draw power from the grid. Due to their fast charge/discharge capability which cannot be achieved by any other mechanical or chemical storage system, SMES are perfect for power quality applications.7 Only limiting factor on response time is the power conditioning circuit. Unlike any other storage system a SMES can hold its charge forever as long as the cooling system keeps the superconducting coil between 4K and 10K.

Batteries

Batteries store energy by going thru a chemical reaction when electrical energy is applied thru them. This chemical reaction can be reversed by putting a load on the battery. Charging batteries takes considerably longer than a charging a capacitor or a spinning a flywheel. In a typical battery cell there are cathode and anode electrodes. The medium between the two electrodes is called the electrolyte. During charge and discharge cycles, ions are carried by the electrolyte between the two electrodes. Batteries can be used in series or parallel, depending on the application, in order to increase voltage or output current respectively and therefore the capacity of the system. Batteries do not discharge as fast as capacitors. A chemical reaction takes place which then starts electron flow on the circuit. While energy from a battery system can be delivered in milliseconds,12 electronics used for grid connection play a big role in the systems ability to correct power fluctuation on grid. Battery storage systems need inverter circuits in order to be attached to AC grid.

Lead-acid batteries are the most mature technology in storage reflecting their long history of development. However, since practically usable and safe lithium-ion batteries have been by Sony in the 90s, they are being developed at a fast pace.13 Lithium-ion cells are becoming the main battery choice of storage systems due to their long life and less maintenance compared to lead based systems.

Flywheels

Flywheel energy storage systems employ a spinning mass at high speeds. While flywheels have been known and used for over a century, applications for energy storage are fairly new. James Pickard was the British inventor who used a flywheel on a Newcomen steam engine in order to produce rotational motion.14 Now for more than 200 years flywheels are being used in almost any reciprocating engine to provide a smoother power output. The most notable application of a flywheel storage unit was the 1952 Gyrobus used in Switzerland. The flywheel installed in this electric bus was charged at bus stops, bringing the rotor to 3,000 rpm and providing about 6 km of driving distance in city traffic.15

There are two types of flywheels; low speed high mass, which rotate up to 6,000 rpm or low mass high speed. High speed composite material rotors spin up to 100,000 rpm when they are charged.11 This high speed rotating mass inside the unit is connected to a motor which also acts as a generator. The motor spins the mass inside the flywheel assembly hence giving it a kinetic energy. The same motor, during discharge works as a generator; it uses the stored kinetic energy on the rotor and to produce electric energy which then goes through inverters in order to make DC. While discharging, high-speed composite material flywheels slowdown from 100,000 rpm to 10,000 rpm.11

The most significant energy loss for flywheels during standby is the vacuum pump; about 25W of power need to be used to keep a 1KWh flywheel ready.11 Another possible energy loss is eliminated by using magnetic bearings so that the system has almost no standby loss. Unlike batteries which degrade after several charge/discharge cycles, a flywheel does not lose its capacity. Flywheels are expected to last over 1,000,000 cycles.10 Flywheel system energy densities are comparable with Li-Ion battery systems; low speed flywheels can provide 5Wh/kg and advanced systems can reach over 100Wh/kg, while a lithium battery is between 100-150 Wh/kg.10 Power densities are also very close; a lithium battery system can be made to provide between 500 to 2,000 W/kg, a high speed flywheel system can be at 1,000 W/kg as well.10

Comparison of Storage Systems

Discharge Duration and Response Time

All four storage systems have response times less than ½ cycle which is necessary for power quality applications. Since these systems are either supplying DC as in batteries and capacitors or have variable output such as flywheels and SMES, they all incorporate a power electronic circuit which inverts or regulates output. Unlike a turbine or generator engine, there is no wait time for ramping; energy is ready to be consumed on demand. Power electronics is the only limiting factor, which keeps response times very low.

Duration of discharge however can be increased by using multiple units. Batteries and flywheels can be grouped to provide minutes of operation; for corrections that require only up to several seconds of discharge, SMES and capacitors are more suitable.16
Energy and Power Density

Table I summarizes important characteristics of different energy storage systems.

**TABLE I: Energy and power densities, system life**

<table>
<thead>
<tr>
<th>System</th>
<th>Wh/Kg</th>
<th>W/Kg</th>
<th>Lifetime [years]</th>
<th>Life time [cycles]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead-acid</td>
<td>30-50</td>
<td>75-300</td>
<td>5-15</td>
<td>1200-1800</td>
</tr>
<tr>
<td>Li-ion</td>
<td>75-200</td>
<td>500-2000</td>
<td>5-15</td>
<td>1500</td>
</tr>
<tr>
<td>SMES</td>
<td>0.5-5</td>
<td>500-2000</td>
<td>20+</td>
<td>100,000+</td>
</tr>
<tr>
<td>Flywheel HS</td>
<td>100</td>
<td>400-1500</td>
<td>20+</td>
<td>100,000+</td>
</tr>
<tr>
<td>Supercapacitor</td>
<td>0.05-5</td>
<td>10,000</td>
<td>12</td>
<td>500,000</td>
</tr>
</tbody>
</table>

System Cost and Lifetime

Due to very low energy densities, SMES systems have the highest kWh cost ranging from $1,000 up to $10,000 per kWh. However, costs should be considered along with expected life cycles from a system. Technically a SMES can be cycled infinite times since there are no chemicals that degrade or mechanical systems to wear. Flywheels have cycle lifeexpectancies from $10^5$ to $10^7$. Since they are simply a rotating mass on magnetic bearings, only wear in systems happens on electronics which requires capacitor replacements every 50,000 hours or 6 years. A summary is shown in Table II.

**TABLE II: Life and cost of short term storage systems**

<table>
<thead>
<tr>
<th>System</th>
<th>System life [years]</th>
<th>Cycle life [cycles]</th>
<th>$$/kW$$</th>
<th>$$/kWh$$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead-acid</td>
<td>5-15</td>
<td>1,200-1,800</td>
<td>300</td>
<td>200</td>
</tr>
<tr>
<td>Li-ion</td>
<td>5-15</td>
<td>1,500</td>
<td>300</td>
<td>250</td>
</tr>
<tr>
<td>SMES</td>
<td>20+</td>
<td>100,000+</td>
<td>1,000</td>
<td>1,000</td>
</tr>
<tr>
<td>Flywheel HS</td>
<td>20+</td>
<td>100,000+</td>
<td>1,000</td>
<td>1,000</td>
</tr>
<tr>
<td>Supercapacitor</td>
<td>12</td>
<td>500,000</td>
<td>300</td>
<td>200</td>
</tr>
</tbody>
</table>

Conclusion

There is no single storage solution; instead a combination of systems should be deployed depending on the needs. In general storage applications depend on location, duration of output, response time, power and energy capacity, installation and running costs of the system. Flywheel technology is not as mature as pumped hydro or even battery back-up systems. However, advancements in their field promise scalable, lower cost, longer lasting and higher energy density storage systems. While still in their early development stages, flywheels have proven to be extremely long life with high cycle efficiency and require little maintenance. They are excellent candidates for wide applications not only in large scale grid storage but also in small system for residential storage.

Electric Vehicle Batteries: Li-ion and Beyond, Challenges and Advancements

Bilash KC
University of Illinois at Chicago, Chicago, IL

Batteries are key to developing affordable Electric Vehicle (EV). However, EVs have not yet come on par with gasoline vehicles in many areas such as price, driving range, and recharge time. Many research areas are actively seeking to improve the current market dominant lithium-ion batteries (LIBs) as well as find alternatives to LIBs. This review will look at current status of LIBs, a few alternatives, and collective challenges and advancements associated with these batteries.

Introduction

An electrochemical battery in an EV provides clean source of energy without Greenhouse gas (GHG) emission and noise pollution that is typical of internal combustion engine vehicles. Resurrection of modern days EVs was initiated by Toyota Motors by introducing Prius Hybrid in 1997 with the Nickel Metal Hydride battery. By 2000, Prius was an international success, and it has been the highest selling hybrid to date. In 2008, Tesla Motors Inc. introduced highway-capable Tesla Roadster with 200+ miles range. In subsequent years, major auto manufacturers such as Chevrolet, Nissan, BMW, Audi, Mercedes and others have introduced their own EVs in response to the growing consumer demand.

The powertrain, especially the battery, is the most important component of an EV, which determines several crucial factors such as mileage range, purchase cost, safety, and convenience of recharge. The battery for an EV is simply the combination of individual battery cells in parallel and/or series. For instance, Tesla Model S uses over 7000 of the readily available Panasonic 18650-type lithium-ion (Li-ion) cells, whereas Nissan Leaf uses 192 individual Li-ion cells designed by Automotive Energy Supply Corporation (AESC). To achieve commercial success for EVs, batteries should have a right balance between storage capacity, cost, lifetime, recharge time, and safety, and LIBs currently hold collective advantage over other alternatives. Consumers want affordable, practical driving range comparable to that of a gasoline vehicle, convenient to recharge, and safe to operate EVs. All these factors are essentially battery related, and thus battery research and development is a key component in determining the rapid growth and success of EV market.

Battery Chemistry

A battery cell is simply a chemical composition of two electrodes and an electrolyte. The choice of electrodes and electrolyte composition, along with the structural design of the cell determine the electrochemical performance, cost, and safety of a battery. For instance, lithium, being the lightest metal and the strongest reducing agent, is unsurprising the most popular choice for positive electrode composition (such as LiFePO₄) to yield light-weight, high energy density batteries. While numerous researches are being carried around the globe for affordable, high density LIBs, alternatives such as Lithium-air (Li-air), Lithium Sulfur (Li-S), and Magnesium ion (Mg-Ion) are also being explored in response to the increasing demand. This paper will look at current market dominant LIBs and a few potential beyond Li-Ion (BLI) successors, in terms of both challenges and advancements. It will also review the cost, range/recharge time, and safety issues commonly associated with these types of batteries.

LIBs

The theoretical density of a LIB is around 400-600 Wh/kg, but the current practical density is around 250-250 Wh/kg (see Figure 1). Although the theoretical energy density is low compared to other cells, for all the practical purposes, LIBs are the leading market leader for EVs. The commercial booming and success of LIBs after the introduction of Sony LIBs by Sony Inc. provided 25 years of head start for LIBs. Energy density for LIBs is increasing at a rate of 5-10% per year which has enabled the commercialization of EVs, but growing energy consumption demands better performing batteries. Modern LIBs have seen only three-fold increase in energy density since the first commercial versions sold by Sony in 1991. Battery researchers believe storage capacity for LIBs is heading towards a saturation limit, and only technological improvements can potentially improve energy density by weight by about 30%. If this is the case, then EVs with LIBs will never achieve mileage range on par with traditional gasoline vehicles. Regardless, research continues to seek ways to achieve LIBs with higher specific energy density of around 400+ Wh/kg (see Table 1).
TABLE I: Gravimetric densities of different cells

<table>
<thead>
<tr>
<th>Cells</th>
<th>Theoretical value [Wh/kg]</th>
<th>Best commercial value available [Wh/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-ion</td>
<td>400-600</td>
<td>≤ 250 (Tesla Motors)</td>
</tr>
<tr>
<td>Li-S</td>
<td>2,600</td>
<td>350 (Oxis Energy)</td>
</tr>
<tr>
<td>Li-Air</td>
<td>7,650</td>
<td>TBD</td>
</tr>
<tr>
<td>Mg-ion</td>
<td>800</td>
<td>TBD</td>
</tr>
</tbody>
</table>

As a result, researchers keep looking for high conductive efficient electrolytes, and the combination of suitable electrodes and electrolytes to avoid such problems, and achieve higher Coulombic efficiency. Promising results in research laboratories on this front have not turned into commercial successes. The results obtained under controlled environments rarely hold up while shifting to large commercial scale for various reasons such as cost, efficiency at large scales, safety issues, and replication of results. For instance, Envia Systems, a battery startup, made big headlines in 2012 claiming a high density EV battery that could deliver 400 Wh/kg, which was about twice what any other batteries could deliver at the time. However, attempts to replicate the results failed. Envia associated the 400 Wh/kg landmark fluke with faulty results created by a contaminant in a batch of electrodes from the suppliers.

Many experts and battery research veterans feel 400 Wh/kg will be impossible to achieve before the end of the decade given the historically slow incremental gain in energy storage density since 1991. Despite some setbacks on commercializing potential LIB breakthroughs, several research groups and major companies are still working to develop LIBs that can achieve this milestone in foreseeable future. Samsung SDI, the world's largest LIB maker, has set a more modest goal of achieving 250+ Wh/kg by 2019. BioSolar Inc., in partnership with the University of California, Santa Barbara (UCSB), is targeting to develop LIBs with 450 Wh/kg by 2016. Tesla Motors, with Panasonic, is building a LIB factory Gigafactory 1 in Nevada, to be operational by 2016, to develop batteries with specific energy density of around 350 Wh/kg.

Although LIBs have greatly assisted the commercialization of EVs, transportation industry demands higher battery performance to challenge the traditional gasoline vehicles dominated auto market. Next-generation BLI batteries those can outperform LIBs in every criteria are needed for global deployment of EVs. The problem, however, lies in the fact that the current battery Research and Development (R&D) largely focuses on trial and error approach rather than the fundamentals of electrochemistry. Envia's failure suggests that a better understanding of battery electrochemistry is favored over going through numerous possible permutations of electrodes and electrolytes composition to achieve desired results. For instance, replacing graphite anode in LIBs with pure sliver of lithium anode will greatly increase the energy density, and also makes the cell lighter and smaller in size. But, this increase in density comes at the cost of safety, and not enough has been done to overcome the challenge. Pure Li anodes suffer from what is called dendritic growth. During the cycling process of a LIB, microscopic fibers of Li-ion (called dendrites) emerge from one anode and keeps growing continuously across the electrolyte solution, and eventually reaches the cathode. When current flows through this dendrite, it can cause internal short-circuit, leading to overheating of the battery, and in some cases fire. This problem remains a challenge for BLI battery chemistries such as Li-S and Li-air, and has yet to meet with success.

**Li-S**

Although research on Li-S rechargeable batteries was originally done in the 1960s, they did not survive past 100 cycles, and subsequent interest in Li-S battery research faded. More than 50 years later, laboratory results have hinted at Li-S battery as one of the potential successors to LIBs primarily because of its theoretically high specific energy density (2,600 Wh/kg) and relatively low cost. In a typical Li-ion cell, the layered graphite electrode occupies a lot of space as a host for lithium ions, whereas in Li-S batteries each lighter sulfur atom can host two lithium ions, allowing for higher storage density. A sliver of pure lithium metal is used to perform double duty as an anode and as a lithium ion supplier. The sliver shrinks as the battery discharges and reforms as it charged (see Figure 2 and 3). These factors create the potential to develop Li-S batteries that are lighter, and have higher energy density. In an positive recent development, a team of researchers from the University of California Berkeley and Lawrence Berkeley National Laboratory was able to retain Coulombic efficiency of over 99.7% after 1500 cycles in Li-S cells, and the team estimates that a commercial version of the battery should deliver around 500 Wh/kg if it goes into production.
Although Li-S batteries seem promising, they have their own challenges. Internal short circuit caused by the dendrite formation remains the most challenging problem. Similarly, reaction between Li and S, during charge/discharge cycles, creates several polysulfide compounds, which, when dissolved into the liquid electrolyte, can diffuse back and forth between electrodes, forming insoluble Li$_2$S (or Li$_2$S$_2$) on the surface of the Li metal electrode, resulting in lower Coulombic efficiency. This problem was addressed using nanofabrication that uses cathode material designed using nanotechnology (core-shell nanostructure comprising Li$_2$S nanospheres with an embedded graphene oxide (GO) sheet as a core material and a conformal carbon layer as a shell (Li$_2$S/GO@C cathode) to avoid this problem and achieve the 99.7% Coulombic efficiency.

Likewise, another research team is addressing the fundamentals of Li-S electrochemistry by looking at theoretical calculations and computational analysis to better understand the sulfur redox chemistry on the electrolyte/ carbon interface by using Raman spectroscopy and density functional theory (DFT). This understanding of fundamental electrochemistry will help maximize the usage of sulfur atoms for higher energy density and cycle stability as the research continues, and commercialization awaits.

There are a few industrial companies standing by LiS battery development. Oxis Energy in Abingdon, UK has been developing Li-S batteries for various applications, and is setting new ambitions for its Li-S batteries use in EVs. It claims to have achieved energy density of 300 Wh/kg in 2014, and aims to reach 400 Wh/kg by 2016, and 500 Wh/kg by 2019. Sion Power, an Arizona-based rechargeable battery manufacturer, has claimed it already developed 350 Wh/kg Li-S cells in 2004 and is planning to develop 600 Wh/kg Li-S cells in near foreseeable future. Sions Li-S battery was used in Airbus Defense and Space Zephyr 7 prototype High Altitude Pseudo-Satellite (HAPS) aircraft in 2014, and the company is planning on releasing a commercial version of the battery for EVs before the end of decade.

Li-Air

Li-air battery has also drawn research interest in past few years because of its high theoretical energy density ($\approx 12,000$ Wh/kg) and practical energy density ($\approx 1,700$ Wh/kg), which is comparable to that of gasoline. A Li-air cell uses the electrochemistry of oxidation of lithium at the anode and reduction of oxygen at the cathode (see Figure 4). A commercial version would potentially be lighter since it uses oxygen as cathode, and also cheaper compared to other conventional batteries.

Research on Li-air Batteries, however, is still at an infancy state and continues to face many hurdles, mainly overvoltage and safety issues. Since the absorption and release of oxygen both happens at the cathode surface, a very large surface is required for higher energy density and cycle stability as the research continues, and commercialization awaits. In addition, to avoid the safety issues arising from Li dendrite in Li-S cells, research groups are also looking at lithium-free anodes such as silicon with prelithiated Li$_2$S based cathode.

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Decrease in cell storage capacity over time, volatility of electrolytes, and suitable porous membrane for the easy inflow of air while still keeping intact the electrolytes etc. are few other challenges hindering the commercialization of Li-air batteries.23,25,26

IBM, in 2009, started Battery 500 Project to develop lighter, cheaper Li-air batteries with ten times the energy density than conventional LIBs that could deliver 500+ miles range on a single charge. In 2012, the Joint Center for Energy Storage Research (JCESR) at Argonne National Laboratory won US $120 million from the US Department of Energy (DoE). JCESRs target was to achieve an EV battery five times energy dense, and five times cheaper than any other currently available batteries. Although Li-air was considered by JCESR to have potential for being LIB successor, slow progress and safety issues of Li-air have refocused their priorities. For instance, efforts to eradicate the persistent dendrite problem with Li-air that cause short circuits and react aggressively with many other contaminants was only met with limited improvements. A research group in 2015 reported success with the preventive measure for dendritic growth in laboratory tests where it found that in situ formed nanostructure-stabilized solid electrolyte interphase (SEI) layers formed from the reactions between Li metal and solvents could prevent dendritic growth.27

Despite the potential risks, major companies are standing by the potentials of Li-air battery. Volkswagen is planning on using Li-air batteries on its EVs within the next decade.28 Despite the initial setback, IBM is still planning to put Li-air battery on EV before 2020.29 Similarly, Samsung Inc. is also planning on bringing 300 Wh/kg Li-air in market by 2020.12

Mg-ion

Another promising alternative for high density rechargeable batteries avoids lithium ion completely and uses heavier elements such as magnesium. Multivalent ions such as Mg-ions provide two electrons for current flow in contrast to just one from Li-ions.30 A Mg-ion battery can, thus, theoretically provide twice the current compared to a LIB under similar circumstances, which leads to theoretical energy density of around 800 Wh/kg.30 It also is cheaper and safer than a LIB.30 However, Mg-ions move very slowly through the electrolyte because of the heavy mass leading to lower Coulombic efficiency and greater charge/discharge time. A group of researchers from JCESR found that the Mg-ions were experiencing heavy drag because they were attracting other ions from the solvents (coordination spheres), and thus making them bulkier. Another JCESR research group through computational simulation suggested that the performance bottlenecks in Mg-ion batteries may be related to what happens at the interface between the electrolyte and electrodes as the Mg-ions shed their coordination spheres.31 Stable, high conductive, and non-

corrosive magnesium battery compatible electrolytes for better flow of Mg-ions and longer cell life are also being explored. For instance, research group at Lawrence Berkeley is using supercomputer simulation of hundreds of different electrolytes to find the suitable combination of electrodes and electrolytes that offers least drag to mg-ions.32 In addition, major electronics firms and automakers such as LG, Samsung, Hitachi, and Toyota are also working on Mg-ion batteries.9

While LIBs and BLI batteries are being explored, the common denominators that determine commercial success are cost, quick rechargeability, and safety. Consumers need to be convinced that EVs can perform on par with the gasoline vehicles, and thus, these three factors are crucial for any battery chemistry and research should be carried in parallel to optimize these factors.

Cost

Battery price is primarily responsible for the higher upfront price of an EV.4 Since most EV batteries are built by combining numerous individual cells, the battery price is determined largely by the cost of an individual cell. Comparing all factors, cathode materials, separators, and electrolytes have been the primary drivers of cost, and ongoing research is actively working to develop cheaper alternatives to existing materials.32 In addition to the individual cell cost, packaging cost, safety features, mass production, and business strategies are also responsible for driving higher prices for batteries. However, as one looks at the past decade, cost ($/Kilowatt-hour) has been significantly reduced, even faster than anticipated, especially for market dominant LIBs (Figure 5). The current price is still not low enough though to make EVs serious competitors in terms of upfront purchase cost.

In their research paper Rapidly Falling Costs of Battery Packs for Electric Vehicles authors Björn & Månsson looked at over 80 different sources between 2007-2014 to get an approximation on the $/KWh for successive years. They found that the cost declined by around 14%
annually, and the reduction had been largely due to reduction of materials cost, mass volume production, and engineering feats. Cost went down between 6-9% for cumulative doubling of production as a result of increase in EV sales. The price fell from around $1,000/KWh to around $400/KWh on average, while market leaders such as Nissan Leaf and Tesla Models S batteries are estimated around $300/KWh. In their research paper Rapidly Falling Costs of Battery Packs for Electric Vehicles authors Björn & Måns looked at over 80 different sources between 2007-2014 to get an approximation on the $/KWh for successive years. They found that the cost declined by around 14% annually, and the reduction had been largely due to reduction of materials cost, mass volume production, and engineering feats. Cost went down between 6-9% for cumulative doubling of production as a result of increase in EV sales. The price fell from around $1,000/KWh to around $400/KWh on average, while market leaders such as Nissan Leaf and Tesla Models S batteries are estimated around $300/KWh. Industrial experts believe that the cost per kilowatt hour should be around $100/KWh-$150/KWh for a battery in order for an EV to be cost-competitive on par with a gasoline car. The fact that the practical limit of energy density used in current LIBs has not increased considerably means that price still hovers around $400/KWh on average. LIBs have room to improve, and possible alternatives have the capacity to deliver better $/KWh needed for commercial success. Although many laboratories results highlight several ways to achieve higher energy density with reduced cost, they often fail to hold on commercial scale. Nevertheless, mass production, cooperate strategy, and incremental engineering improvements in batteries have brought cost relatively down in past few years. It is most evident in case of Tesla Motors, which probably has the best $/KWh numbers in business. It has managed to increase energy density by more than 50%, and cut the price almost in half since its first launch of Tesla Roadster in 2008. Tesla Model S battery delivers 250 Wh/kg compared to around 100-200 Wh/kg for most others EVs on the market for a cost of under $300/KWh, and this cost reduction has not been due to radical improvement in LIB chemistry, but has come through engineering improvements such as battery packaging design, battery integration in vehicle, and cost effective safety materials.

DoE’s role in falling price

Realizing the future potential of EVs, DoE has invested in funding to the development of better and cheaper batteries. DoEs Vehicle Technologies Office (VTO) partnered with United States Automotive Battery Consortium (USABC) in 1991 to support the technological advancements of EV batteries. DoE invested around $315 million during 1992 - 2010 in R&D of affordable commercial batteries, especially LIBs during the later years. As a result of the collaboration, DoE claims that three USABC battery developers were able to increase the energy density by 60%, and reduce cost by 70% from around $1,000/KWh in 2008 to current cost of $289/KWh as of now. In 2009, DoE announced $2.4 billion in grants to several projects under the American Recovery and Reinvestment Act of 2009(ARRA) to accelerate the development of EV batteries and put the U.S. in the forefront of emerging EV market. In 2012, President Obama launched EV Everywhere Challenges as a part of Clean Energy Grand Challenges to offer affordable EVs to consumers with a decade. Argonne National Laboratory (ANL), National Renewable Energy Laboratory (NREL), and USABC are few big partners helping DoE achieve its target.

Mileage and Charging Rate

Most EVs still offer less than 100 miles range on a full charge, which is a discouraging factor for owners and potential buyers who are frequent travelers and long distance commuters. In addition to lower range, the recharge time is not all that impressive as well, and most of the EVs take well over hours (5+ hours - overnight) for full recharge. Range-anxiety (the fear that an EV will run out of power before reaching the next available charging station, and thus, leaving the vehicles occupant stranded) of owners and potential buyers can be eased with the development of quick recharging batteries with longer range.

Charging time vary depending upon the battery type, battery capacity, battery depletion amount, types of charger, external temperature, and several other factors. When an external charging source is connected to the battery pack, the reversal of electrons and ions flow takes place until the desired electric potential of the battery is restored. On cellular level, the unwanted results of electrochemistry such as drag force on ions, heat generation, and compounds deposition on electrodes decrease the Coulombic efficiency and increase the recharge time. The charge/discharge rate is thus largely determined by the chemical composition of electrodes and electrolytes, electrodes geometry, porosity of the electrodes and surface layer coating (see Figure 6). On the engineering side, nanoengineered electrodes with high porosity and the high surface area means greater number of ions flow, and faster recharge time.

Amongst all, the most limiting case for recharge process is the intercalation of ions into electrodes where the ions have to overcome an energy barrier at anode. Typical LIB electrodes (e.g. graphite anode and LiCoO2 cathode) exhibit low diffusion rate of Li-ions compared to lithium salt electrolytes (e.g. LiPF6), leading to slow recharge. On the other hand, cycle-induced and time related factors such as consumptions of ions by SEI, polarization resistance, high voltage saturation etc. lead to capacity loss, lower coulombic efficiency, and longer
recharge times. For researchers wanting to cut down the recharge time, the focus has been on using the engineered nanostructures of electrodes (electrode nanoarchitecture) such as uses of inverse opal geometry for anodes (to achieve higher surface area, and thus higher diffusion rate and higher intercalation of Li-ions), and suitable chemical composition of electrodes and electrolytes for easy transportation of ions.

Since charge/discharge process is regulated by the intercalation of Li-ions in anodes, anodes with higher intercalation rate, and increased diffusion rate are being looked at through experiments and simulations such as Molecular Dynamics (MD) and Monte Carlo (MC). For instance, researchers simulated the charging process of LIB and found that applying oscillating voltage reduced the intercalation time of Li-ions into graphite anodes, and increased the diffusion of Li-ions into electrolytes, significantly decreasing the recharge time. Similarly, modern day nanofabrication techniques to develop high capacity anodes are also being researched, especially silicon since it has higher specific capacity (3580 mAh/g) compared to traditional graphite anodes (372 mAh/g). However, Si has relatively low conductivity, and also suffers from pulverization due to continuous expansion and contraction during the intercalation and deintercalation process, resulting in capacity reduction.

To get rid of pulverization problem, high strength porous Si-based anodes could be nanostructured that could support the volume expansion of Si. Such methods include developing electrochemically grown 3D porous inverse opal structure of Si@Ni (Si electrodeposited into Ni scaffold allowing Si volume expansion with reduced stress, and also higher diffusion rate and better conductivity), and nanoengineered porous carbon black (CB) cage with conducting CB networks (Figure 6) that encapsulates Si (while CB cage reduces the stress on Si and provides expansion volume while maximizing surface area at the same time, CB networks enhance the electrical conductivity). At the same time, stable, non-corrosive, high conductive electrolytes those can increase intercalation rate are also crucial for fast recharge. For instance, high concentration of lithium salt (LiN(SO2F)2) in 1,2-dimethoxyethane (DME) ether solvent was found to result in even faster intercalation rate of Li-ions into graphite anodes compared to the commercially used ethylene carbonate electrolytes. As usual, these are all the laboratory successes results, and commercialization awaits.

Safety

All batteries should pass the governmental safety regulations before they could be put out in EVs and brought to market. Safety issues come in variety of forms from internal electrochemical safety failures to external abuses. The most recent headlining news would be the two Boeing 787 Dreamliner Li-ion batteries that caught fire, one in air in Japan, and other on ground in Boston. For the latter one, National Transportation Safety Board (NSTB) found a short circuit in one of the cells to be the most likely cause. Few other safety incidents that have caught public attention in recent years are battery ignition after crashes in Model S, battery pack ignition at assembly plant of Mitsubishi i-MiEV, and short circuit in battery pack of BYD e6 after crash. Few common safety concerns commonly associated with all types of battery chemistries are discussed below.

Electrical and Thermal Failures

As discussed before, dendrite formation is one of the major safety issues with Li-air and Li-S batteries. Dendrites cause internal short circuits, leading to overheating and, at times, ignition. Similarly, overcharge, overdischarge, overcurrent flow, low temperature charging (below 0°C) all generate unwanted exothermic reactions resulting in temperature rise (which might overcome the cooling efficiency of the battery), thus leading to overheating and potentially, ignition. This process, in addition to heat from internal resistance, might trigger series of uncontrolled electrochemical reactions, eventually leading to what is called thermal runaway, which might even lead to rupturing of battery. Laboratory research has shown promise in solving the short circuit problem. The use of nano-engineered anode materials is one method to avoid the dendrite formation. Another
method involves including temperature-responsive microcapsules that can be embedded internally in LIBs, which will self-extinguish the fire if ignition occurs. Similarly, using biphenyl as polymerizable electrolyte additive can help protect the batteries from overcharge.

### Mechanical Failures

Factors such as vibration, crush and penetration might lead to potential dangers of chemical exposure, thermal runaway, electric arcing, and fire ignition in batteries. Even if no safety risks occur, battery performance could drastically reduce due to the damage of components. Safety requirements for hazard prevention against mechanical abuse should include prevention of electrodes disintegration due to volume changes during cycling process, breakage of electrodes under shock, integrity of cells connectors, and prevention of electrolyte leakage. Battery penetration by sharp objects during crashes should be avoided by adding protective layers of materials. For instance, in 2014, Tesla Motors added additional protective layers to its battery pack with aluminum and titanium plates to deflect and/or absorb debris from the road during high-speed impact after a Model S vehicles caught fire upon hitting the debris on road. Since mechanical deformation can potentially lead to short circuit, computational and experimental research on the dynamic behavior of batteries upon crashing should be done to understand the mechanical properties of batteries depending upon the size, shape, packing design, shield materials strength, and shock absorption coefficient. Similarly, use of thermoresistant electrolyte that can perform under mechanically deformed batteries without short circuit, such as nanaarchitectured Plastic Crystal Polymer Electrolytes (N-PCPE) could avoid hazard in the unfortunate events of collisions.

### Conclusion

At present time when environmental pollution, global warming, and fossil fuel independence are making headlines, EVs are catching global attention as potential replacers of conventional gasoline vehicles. LIBs greatly assisted in the modern resurrection of EVs. Twenty five years of head start has made LIBs commercially dominant batteries in EVs. However, practical density of LIBs reaching towards saturation, and the increasing performance demand for EVs call for BLI alternatives. Potential successors of LIBs which hold high energy density such as Li-S, Li-air, and Mg-ions batteries are at the forefront of next-generation batteries research. These alternatives have their own challenges to overcome, and require optimization of storage capacity, cost, quick rechargeability, and safety to become commercial successes, and make EVs get on par with gasoline vehicles in foreseeable future. As of today, batteries remain the most important and challenging component for EVs. High energy density and low cost has been the holy grail of battery research. Researches are making gradual improvements in battery performance by incorporating the interdisciplinary branches of physics, chemistry, computational science, and engineering, evidenced by the increasing density, falling cost, and safer batteries. Although commercialization of many encouraging results from laboratory successes awaits to advance the current state of batteries, the future surely looks bright for EV market as indicated by the gradual improvement of battery technology. The success or failure of an EV hinges upon its battery performance. And much has yet to be done to make EV market a global success to which battery performance is quintessential.

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