Addressing the Grand Challenges in Energy Storage

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Electrical energy storage has become an important topic of discussion and debate for both automobiles (transportation) and electrical grid (stationary) applications. The objective of this Special Issue on Energy Storage, with J. Liu, V. Srinivasan and K. Amine as the guest editors, is to provide a comprehensive and balanced view of materials chemistry and materials challenges for a wide range of technologies and applications from transportation electrification to the utility grid. The paper by Liu et al. gives a detailed analysis of the energy storage landscape and status of the materials and technologies, which is followed by review articles on important technologies and featured research articles that include the latest advances in leading groups from the international community. Materials science and materials chemistry play a key role, but energy storage is also a system problem that involves many other issues. Some of the key challenges include:

(1) Analysis and understanding the economics of specific technologies for different scales/different applications to guide technology integration;
(2) New materials, new materials chemistry and electrochemistry, and development of electrolytes to greatly improve the compatibility and performances of the whole system;
(3) Safety and reliability, and the perception of safety;
(4) Revolutionary designs, concepts and architectures that can significantly reduce the system and maintenance costs of large energy storage systems;
(5) Novel energy storage mechanisms, energy storage technologies that are environmentally benign and extremely low cost.

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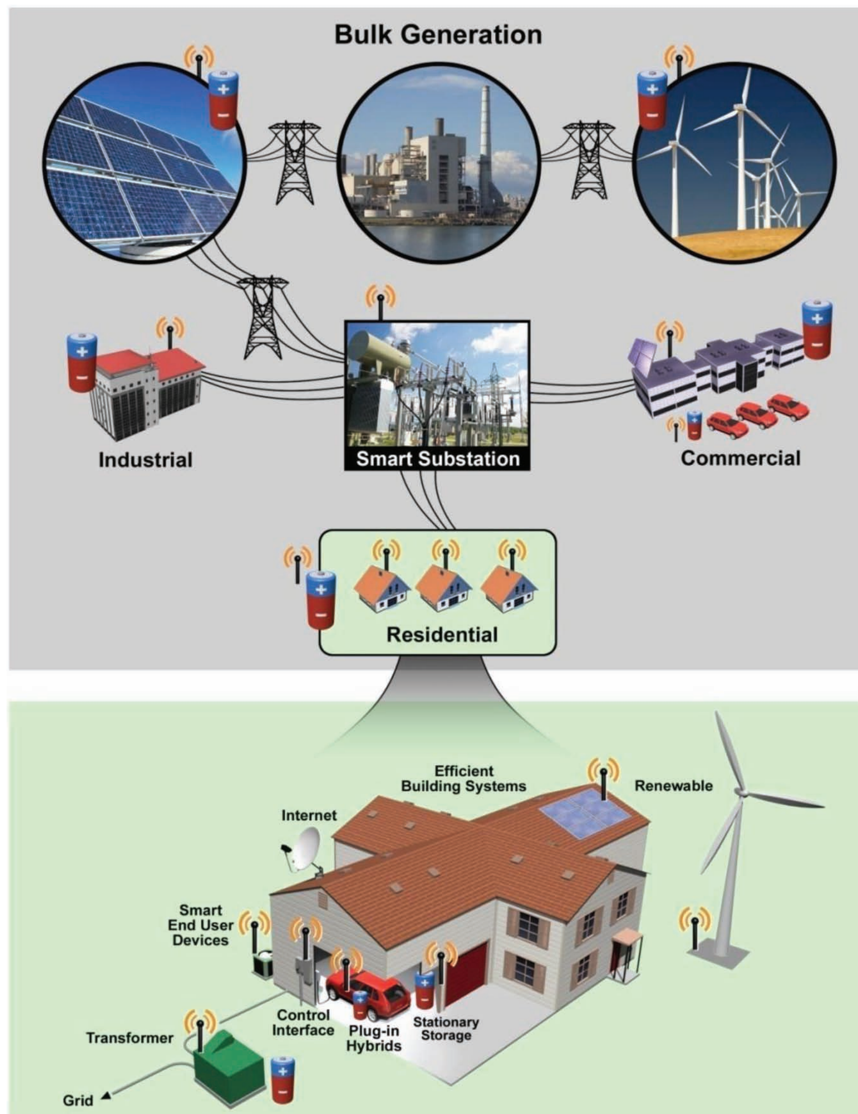

Figure 1. Future smart power grid. Energy storage could improve the perfromance of the power grid, facilitate wide spread use renewable energy on different scales, and enable transportation electrification and integration with the grid.[5]

The vision for future energy infrastructure includes a smart power grid with significant penetration of renewable energy on different levels and the ability to charge and discharge millions of electrical vehicles on the grid (**Figure 1**). Energy storage and conversion is the key enabler of the future power grid. The goal for the US Department of Energy (DOE) and the automobile industry is to develop a battery

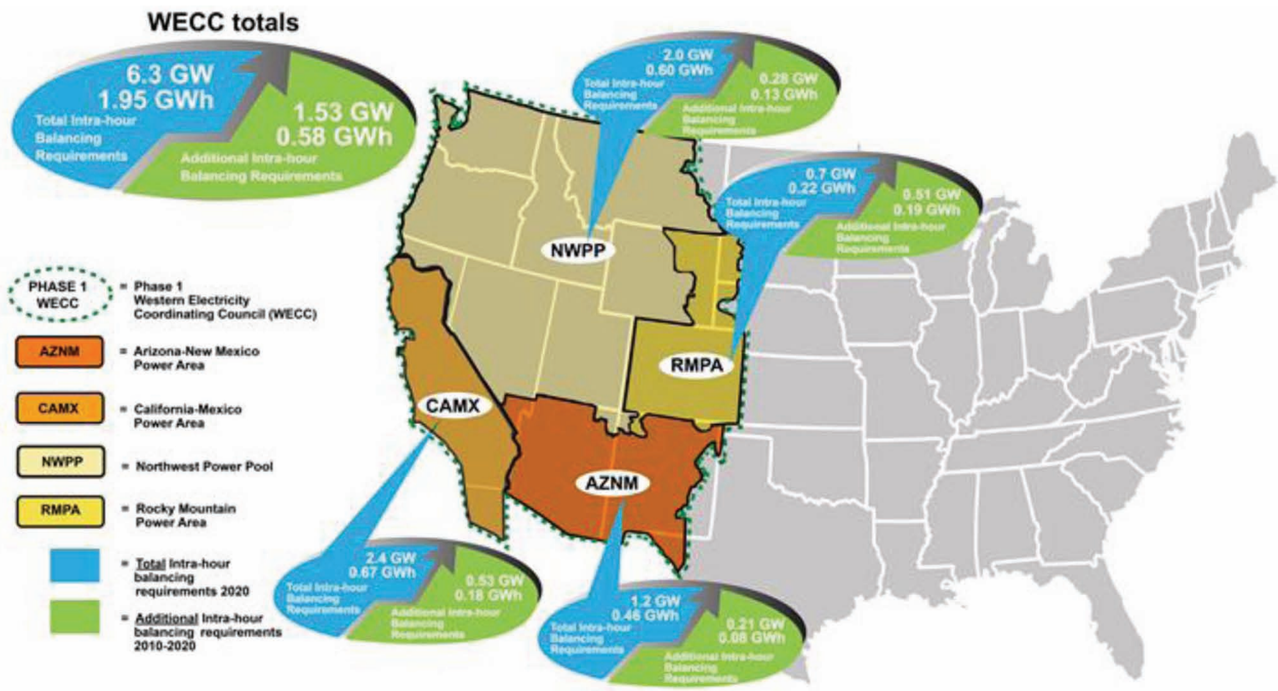

Figure 2. Intrahour balancing requirement for energy storage for the Western Electricity Coordinating Council (WECC) in 2020 with 20% renewable (wind) contribution. The total balancing requirement assumes the displacement of the current technology, and the additional balancing requirement is due to the introduction of new wind capacity.[4]

with volumetric and gravimetric energy densities of 300 Wh/L and 250 Wh/kg, respectively, and a cost of $125/kWh in order to enable the 300-mile range mid-sized sedan. Li-ion batteries have been the prime candidates, and have had huge success in the consumer electronic market in the last ten years, but the commercial progress in the automobile industry is much more challenging. On one hand, the industry has successfully developed a few generations of hybrid electrical cars such as the Toyota Prius, plug-in hybrids like the Volt by General Motors, all electric cars like the Nissan LEAF, and a whole generation of all electrical taxi fleets in China. On the other hand, the electrical vehicle market and the public interest are still fragile and fluctuate with the economy, and large industrial investment fails to succeed in the market place. The development of long range electrical vehicles hinges on the development and commercialization of high energy cathode and high capacity anode materials such as the Li-rich Mn-based layered composite cathode and silicon anode. The long-term stability of those materials, however, still needs to be improved. Significant breakthroughs are needed to meet the performance requirements. This Special Issue invited experts from leading groups in the world to discuss the status and progress in this important field. Chen et al. summarize the important progress in the field of nanostructured titanium based anode materials. Noh et al. discuss the latest progress in developing high capacity core-shell cathode materials with greatly improved cycle life. Papers by Pērez et al. and Byon et al. report new results on methods to produce novel carbon architectures which have good potential for anodes in Li-ion batteries and electrodes for supercapacitors. The role of the electrolyte is becoming increasingly important, but has attracted much less attention. This Special Issue also includes one paper by Lee et al. on composite gel electrolytes with Li powders as the anode. Finally, Nam et al. report new results on using in situ X-ray diffraction and absorption to probe the structural evolution of high capacity cathode materials during operation. Such new tools, including the recent development of in situ transmission electron microscopy (TEM) techniques developed by the Pacific Northwest National Laboratory and Sandia National Laboratories,[1–3] provide a new window to directly observe how a battery behaves on the atomic and nanometer scales.

Safety is a top issue for energy storage. Any safety problems, or perception of safety problems, can significantly delay the development and implementation of the technology. There have been already a few incidents involving Li-ion battery powered electrical vehicles. Although the exact causes and problems are still under investigation, the public perception can play an important role in the support of the new technology. It is anticipated that there will be great emphasis on the research efforts to improve the safety of energy storage devices, such as the development of safe electrode materials as exemplified by the titanate anode (Chen et al.) which has excellent stability and fast charge discharge rate, and does not produce Li dentrides that causes

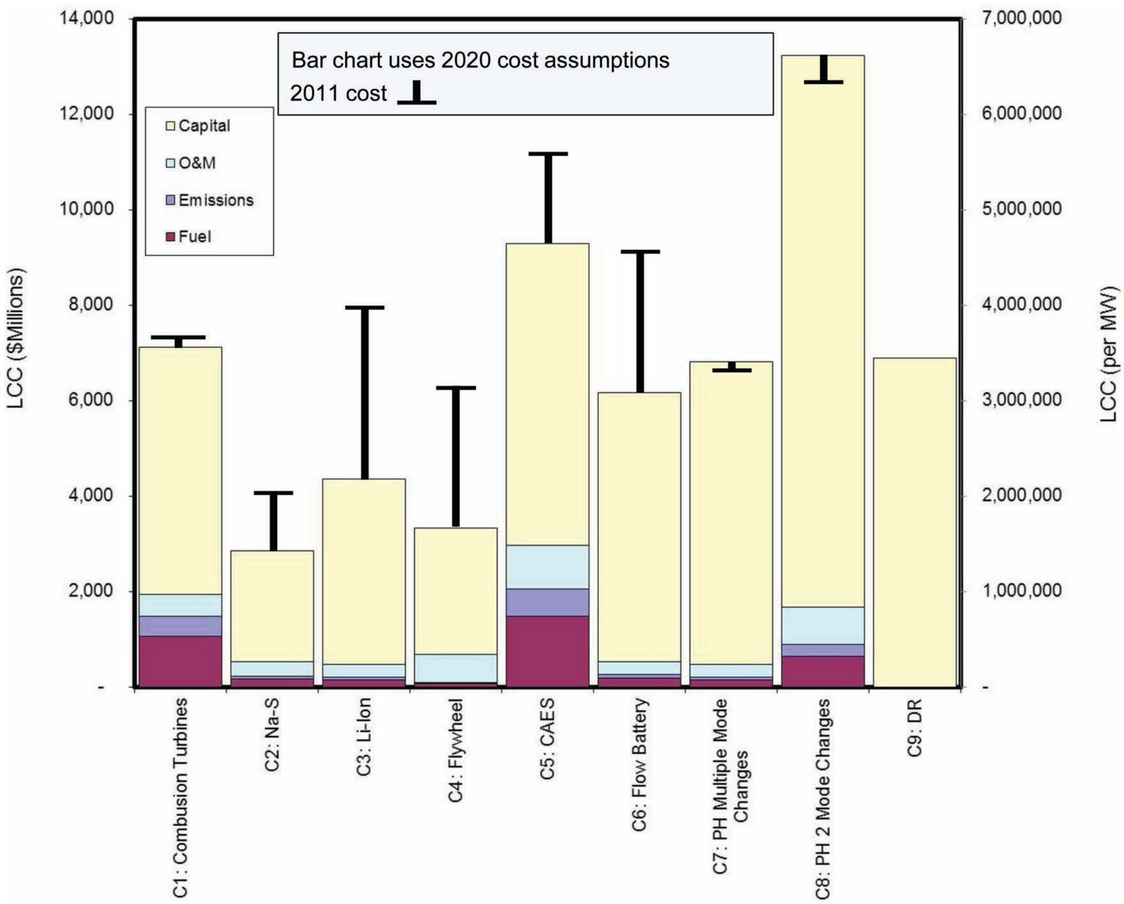

Figure 3. Total life cycle cost of different technologies for intrahour balancing requirement in the Northwest Power Pool (NWPP).[4] O&M: operation and maintainence cost. CAES: compressed air storage. PH; pumped hydro. DR: demand and response.

electrical shortage. The electrolytes are even more important for battery safety. One approach is to develop semi-solid electrolyte (gel electrolyte) that are much more stable and resistant to electrical and mechanical damage (Lee et al.). Another approach is to develop solid electrolytes for all-solid-state energy storage devices, but such efforts are still under intense investigation due to the lower conductivity of the solid-state electrolytes along with the integration of the solid electrolyte into the system. Still, companies such as Toyota are beginning to show great interest in such solid state devices.

There has been growing interest in developing materials and technologies that have much higher energy densities than what Li-ion batteries can achieve theoretically (so called "beyond Li-ions"). Two potential technologies, Li-S batteries and Li-air batteries have received the widest attention. Li-S and Li-air batteries have theoretical specific energies of 2600 Wh/kg and up to 12 000 Wh/kg (based on the Li anode), respectively. These technologies suffer from poor reversibility and slow reaction kinetics due to the poor stability of the electrode materials, irreversibility of the interfacial reactions, and aggressive interactions with the electrolytes. In this issue, Shao et al. provide a good review of the status and problems in non-aqueous Li-air systems. Lin et al. report new results on using additives to dissolve the irreversible reaction products and passivate the metal anode to improve the performance of the Li-S batteries. Kim et al. designed new carbon-sulfur composites, and new electrolytes to improve the conductivity and reduce sulfur dissolution. Still, the fundamental reaction pathways and mechanisms in Li-S and Li-air batteries remain poorly understood. There is great concern and debate on the practical energy density that can be achieved. In Li-S batteries, the most attractive approach to using porous carbon to confine the sulfur will greatly reduce the overall energy density. In Li-air batteries, the use of porous carbon cathodes, the precipitation of the reaction product, and the need to use specialty membranes, packaging materials, and auxiliary mechanics to make the battery work will also significantly reduce the overall energy density.

There are many other important issues that the Special Issue does not discuss due to limited space. For electrical vehicle to work, the batteries need to be charged and discharged rapidly, depending on how the electrical vehicle is used. Fast charge on the road needs to be accomplished in a matter of minutes, rather than hours (with a rate greater than 10C). Such high speed charge/discharge cannot be accomplished with currently known chemistry. Most electrode materials simply do not have such rapid charge and discharge kinetics. For example, the common graphite materials used as anodes, can be rapidly discharged, but cannot be rapidly charged due to the slow motion of the Li-ions into the interlayer spacing. Attempts to force the Li-ions into the graphite material rapidly will inevitably cause Li metal plating on the anode surface which leads to dendrite formation on the anode and failure of the device. Even if the electrode problems can be solved, the management of the power control and charging devices will be very difficult. However, if the vehicle is charged at home, the extra-fast charge rate is not necessary. The Li-ion batteries can tolerate 1C or 2C charge rate which results in less than a few hours of total charge time. Alternative approaches are being explored in other countries, such as battery swapping, but this approach is also difficult because different automobile companies and battery manufacturers are using different devices with different specifications. There seems to be little driving force for the industry to adapt unified standards right now.

The performance requirements for the transportation and stationary storage areas can be quite different. For energy application on electrical grid, the cost needs to be even lower, to the low \$100s/kWh range to achieve the target of 20% wind contribution to the grid by 2030. The stationary energy storage market also covers many applications that range from KW to MW and GW systems and it is not possible for any single technology to solve all the problems. There is still intense discussion in the scientific community on what kind of technologies are needed for what applications, and how much energy storage is needed for these applications. Many of the discussions in the literature are based on large assumptions and educated guesses. Recently, the DOE sponsored a careful study of the energy storage needs for the western states for intrahour balancing requirements.[4] This study for the first time quantified the energy storage capacity needed to displace current spinning reserve (back up energy production) used for balancing the grid and for the added 14 GW wind capacity planned for the near future and concluded that the total requirement of such applications ranges from 3% to 5% of the peak load or 7% to 22% of the added wind capacity.

Some technologies such as Li-ion batteries and supercapacitors developed for the transportation industry could also be applicable for power grid enhancement, but large-scale energy storage technologies are needed to allow for optimum use of existing and new energy assets, improving the reliability of the electricity supply, and for supporting the integration of large-capacity, intermittent renewable energy resources. Besides compressed air and pumped hydro electricity, which are not covered in this Special Issue, the leading technologies being investigated include redox flow batteries and sodium-sulfur (Na-S) batteries. In this Special Issue, Wen et al. provide a systematical review of the development of Na-S batteries, and Wang et al. provide an overview of the latest progress in redox flow batteries, with particular emphasis on the mixed electrolyte vanadium redox batteries which can increase the energy density by more than 50%. Many other hybrid flow battery concepts explored recently are not covered in this Special Issue. Na-S batteries have been in commercial production since 2002, and have been successfully used in many pilot projects in the US, Japan, and China, but a recent fire accident has caused a great safety concern.

The successful development and implementation of energy storage technologies in the grid market depend on the significant reduction of the cost of the technology, the cooperation between the policy makers, the utility companies, and the battery manufacturers, along with a good understanding of where, when, and how the storage technology can be used. Extensive analysis suggests that most technologies are still too expensive right now. However, in the same report from the DOE sponsored study, it was concluded that for intrahour balancing requirements, Na-S batteries (assuming the safety issue can be overcome) and flywheels, pumped hydro and demand-response can be cost competitive today if the whole life cycle cost is considered.[4] Li-ion batteries and redox flow batteries could be cost competitive in the near future with further improvement of the technology. Most technologies are not cost effective for arbitrage (energy distribution based on pricing difference).

Currently, most studies are considering the applications from the grid utility side, which is the largest market. However, the large grid also sets the bar quite high for market entry because of the complexity of the grid and the difficulty for it to adapt to new technologies. At the same time, there are many other applications where energy storage is already used, although not in an effective way. This market includes off-grid applications, end users of PV (photovoltaic) technologies, and distribution and community stations. Currently the most widely used technology is the lead-acid battery. There is no wonder that lead-acid batteries still occupy more than 60% of the total battery market now and the market share has not been reduced by the rapid development of Li-ion and other technologies. There is also great potential to further increase the lifespan and other properties of lead-acid batteries through use of lead-carbon technologies (Liu et al.). Taking the PV market as an example, the Si module price is already approaching \$1/W. The installation price is two to three times the module price, including the energy storage device, which in most cases is a lead-acid battery. If the installation price can be further reduced, it is possible that a 5 kW home PV system will cost less than \$10 000. Currently, the lead-acid battery is still the leading candidate for such applications. The cost of most other technologies is too high and will significantly increase the total system cost. Although one can argue that the total life span cost could be different if the lead-acid battery is maintained and replaced periodically, the initial installation cost could be still the prime concern for the customer.

However, lead-acid batteries are not an ideal technology not only because of the limited life span and the charge/discharge problem, but also because of the environment concern of lead itself (manufacturing and recycling). Even though lead-acid batteries are almost 100% recycled in the US, there is great resistance to the wide spread use in large scale applications in many parts of the world. In 2011 China closed 90% of the lead-acid manufacturing plants. This situation calls for the development of alternative, environmentally friendly technologies with cost comparable to lead-acid batteries. If such technologies can be developed, there is an immediate market to capture right now, and this could further spread to grid level applications in the near future. One example is sodium ion (Na-ion) battery (review by Slater et al.). Na-ion batteries work in a similar principle as Li-ion batteries, except that the Li-ion is replaced by the Na-ion. Unlike Li, Na is of abundant supply, and its ionic form is environmentally friendly, and therefore Na-ion batteries could be potentially much cheaper than Li-ion batteries. However, the Na ion is much larger than Li-ion, meaning it is difficult to move Na ions in the electrode materials. Slater et al. summarize the recent progress in this area noting that there is evidence that real, practical Na-ion batteries will be developed in the near future. The key in the development of such emerging technologies depends on the joint effort of the materials science and materials chemistry community that drive the understanding and development of novel materials and architectures with unprecedented capacity, stability and fast kinetics, and the experts in battery design and manufacturing who can successfully integrate the materials and components in practical devices.

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[1] C. M. Wang, W. Xu, J. Liu, D. W. Choi, B. Arey, L. V. Saraf, J. G. Zhang, Z. G. Yang, S. Thevuthasan, D. R. Baer, N. Salmon, *J. Mater. Res.* **2010**, *25*, 1541–1547.
[2] C. M. Wang, W. Xu, J. Liu, J. G. Zhang, L. V. Saraf, B. W. Arey, D. W. Choi, Z. G. Yang, J. Xiao, S. Thevuthasan, D. R. Baer, *Nano Lett.* **2011**, *11*, 1874–1880.
[3] J. Y. Huang, L. Zhong, C. M. Wang, J. P. Sullivan, W. Xu, L. Q. Zhang, S. X. Mao, N. S. Hudak, X. H. Liu, A. Subramanian, H. Y. Fan, L. A. Qi, A. Kushima, J. Li, *Science* **2010**, *330*, 1515–1520.
[4] M. B. P. Kinter-Meyer, W. Colella, M. Elizondo, T. Nguyen, V. Viswanathan, Y. Zhang, in *Book National Assessment of Energy Storage for Grid Balancing and Arbitrage: Phase 1, WECC* Ed: M. B. P. Kinter-Meyer, Pacific Northwest National Laboartory, Richland **2012**.
[5] Z. G. Yang, J. L. Zhang, M. C. W. Kintner-Meyer, X. C. Lu, D. W. Choi, J. P. Lemmon, J. Liu, *Chem. Rev.* **2011**, *111*, 3577–3613.