Large Scale Integration of Renewable Electrical Energy into the Electrical Grid

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Abstract: Electrical energy is the most consumed form of energy in the entire world. However, the primary way to produce electrical energy is from fossil fuels. Incorporating renewable energy as a replacement to fossil fuels is becoming increasingly important. Unfortunately, direct incorporation of renewable energy leads to blackouts. An efficient method to store electrical energy is required to prevent blackouts and allow renewable energy to be incorporated into the grid. Of the available technology, Li-ion batteries have emerged as a potential candidate for this purpose. However, high cost and safety are concerns that prevent global-scale installation of Li-ion batteries. Redox-flow batteries have recently gained attention as a potential alternative to Li-ion batteries. Because of their design, redox-flow batteries are safer and inexpensive compared to their counterparts.

The growing, global demand for electrical energy has increased research efforts towards the integration of renewable energy sources into the electrical grid. Generation of energy from petroleum-based sources dominates the current market, but dependence on renewable energy is expected to rapidly grow.[1] For example, photovoltaic installations have outpaced annual predictions and are approaching terawatt scales at prices <$0.50/W.[2] However, many issues Their associated with renewable energy impedes their full integration into the electrical grid. One hour of direct solar radiation satisfies the energy requirement for one year.[3] However, direct integration of renewable sources would destabilize the grid leading to power outages and blackouts.[4]

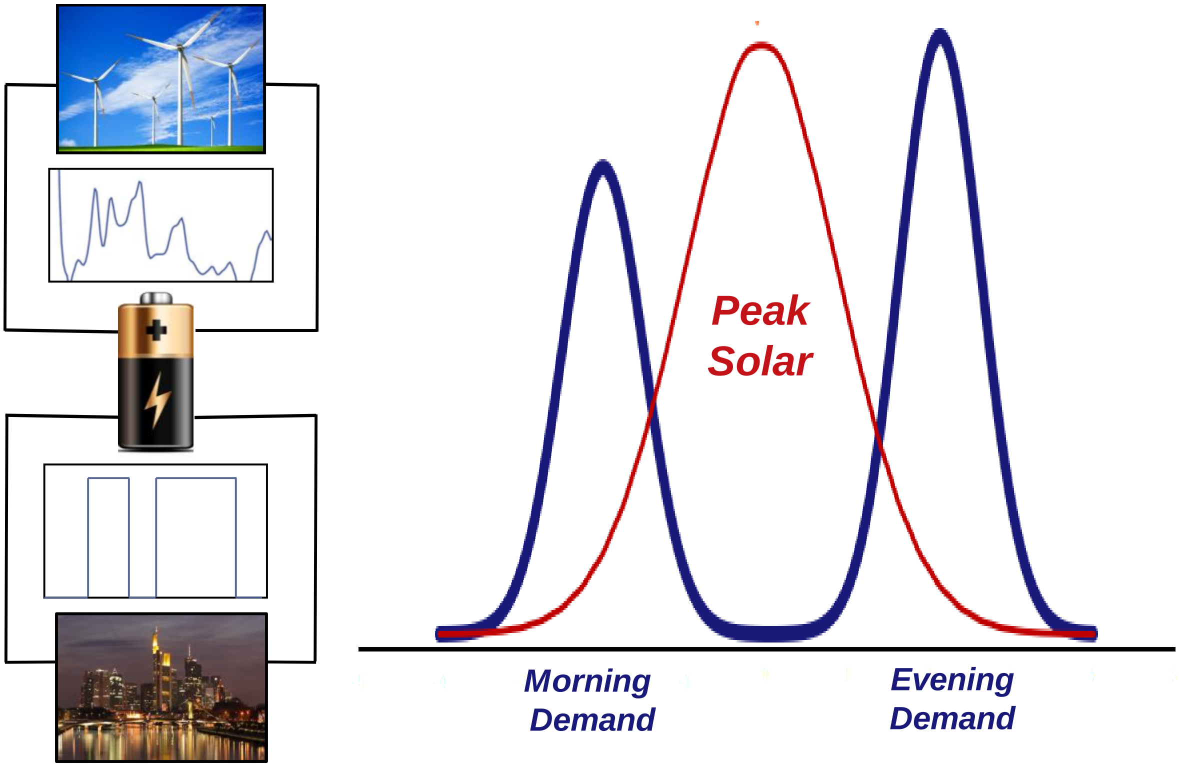

Figure 1: Illustration of EES stabilizing the electrical grid (left). Supply-demand mismatch between energy demand and peak solar sources (right).

Furthermore, harvesting renewable sources are met with the challenges of intermittent renewable sources, difficult transport to load centers, and a supply-demand mismatch. Varying weather conditions greatly affect the availability of solar and wind sources. The amount of harvestable, renewable energy changes by the hour, which would cause influx of energy to the grid to be unstable. This variability causes renewable farms to be localized to areas that are exposed to the greatest solar and wind sources. Farms are located far from most load centers, adding to the difficulty of large-scale integration of renewable sources.[3] Finally, the demand for electrical energy is often at a mismatch with the availability of such renewable sources. During high demand periods, access to renewable sources are at a minimum (Figure 1, right). An example of this supply-demand mismatch of renewable energy is the Jiuquan wind farm.[5] With more than 7,000 wind turbines, this wind farm has the capability to store enough energy to power a small nation. Unfortunately, about sixty percent of the wind farm remains unused because there is not enough energy being used on a daily process. Inexpensive, high capacity electrical energy storage (EES) is required to stabilize the grid and manage issues associated with direct integration of renewable sources (Figure 1, left).

Ideal grid-scale EES technology needs to be scalable and respond quickly to fluctuations in the grid. Supercapacitors is a potential EES technology because of their high life time and quick discharge times.[6] However, low energy density and high cost make supercapacitors an unrealistic candidate for grid-scale storage. Batteries have been targeted as a potential candidate for grid-scale storage, due to high energy densities and the potential to cheaply scale the technology.[3] Of the available technology, Li-ion batteries have been identified as the most "market-ready" with energy densities at ~250-300 Wh/kg.[7] Tesla's CEO Elon Musk made recent headlines when he announced that he was funding the world's largest Li-ion battery in South Australia. The 129 MWh battery was built in conjunction with the Hornsdale windfarm to incorporate renewable energy into Australia's electrical grid.[8] Although a significant achievement in grid-scale integration of renewable sources, Li-ion batteries still have their drawbacks. The first concern is the high cost of scaling Li-ion batteries for grid-scale purposes. The Tesla battery costed $90.6 million, which calculates to a cost of ~$702 per kWh. Economic targets set for grid-scale storage by the Department of Energy's (DOE's) Office of Electricity Delivery and Energy Reliability is set at $150 per kWh. The more aggressive goal of $100 per kWh was set by the DOE's Advanced Research Projects Agency-Energy.[9] In order to fully commercialize Li-ion batteries for grid-scale storage, significant reductions in cost are required. Another drawback is safety concerns with Li-ion batteries. Li-ion technology has been prone to short-circuits, which result in ignition of the battery. In South Korea, LG Chem and LG CNS were responsible for fifteen Li-ion battery-related fires in 2018.[10] At such large-scale, concerns for safety will preclude installation of such technology.[7]

Many alternatives to the typical Li-ion battery have been heavily researched as an alternative to large-scale energy storage. One such example is the utilization of sulfur as an alternative to the classical cathode materials used. Sulfur offers many advantages compared to typical other electrode materials because it is inexpensive and can store a high amount of energy per kilogram of material.[11] However, Li-S batteries performance suffers greatly from what is known as the polysulfide shuttle effect. When the sulfur is reduced at the cathode, large lithium polysulfides are generated and migrate towards the lithium anode during the process of charging. During that migration period, the large polysulfides are reduced to smaller polysulfides that can then shuttle between the two electrodes.[12] Unfortunately, these polysulfides are a result of not fully charging and discharging the sulfur material. This leads to an overall underutilization of the sulfur, which results in decreased battery performance below that of the conventional Li-ion battery.

Aside from replacing the cathode material in lithium-based batteries, research has also looked at replacing the lithium altogether. One main reason for the high cost of lithium batteries

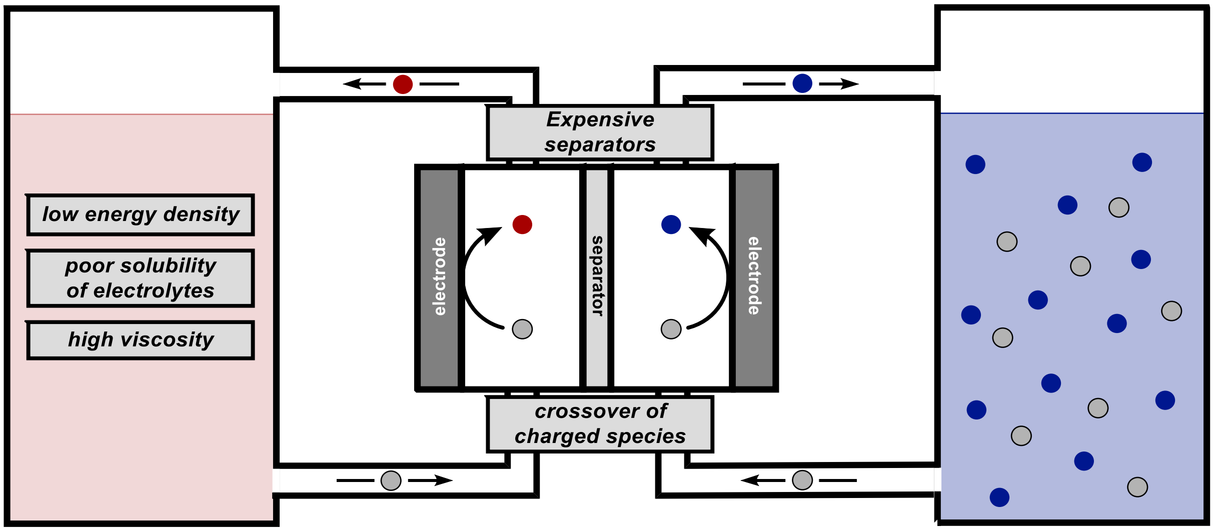

Figure 2: Illustration of RFB with highlighted issues.

is the limited global supply of lithium.[13,14] As an alternative, sodium metal is largely abundant and has similar properties to lithium. Through utilization of a sodium cathode, the price of Na-based batteries is lower than that of a typical Li-ion battery. Although cheaper than Li-ion batteries, Na-based batteries will still be too expensive for global integration of renewable energy sources into the electrical grid.

Redox-flow batteries (RFBs) are an alternative EES technology that is a safer and inexpensive option compared to Li-ion batteries. Unlike solid-state batteries that necessitate direct surface contact between storage material and electrode, RFBs flow solutions of solvated redox-active compounds from external reservoirs to the electrode surface. Mobilization of the storage material decouples battery power (electrode surface area) from capacity (reservoir volume), which renders RFBs inexpensive to scale.[15] The inherent design of RFBs offers the potential for the lowest maintenance costs of any EES technology.[16] Commercial RFB technology utilizes vanadium-based electrolytes in an aqueous environment with stable cycling over 1000 cycles. However, high costs (>$300 per kWh) and low energy densities (<50 Wh/kg) limits the commercialization of most RFB technologies.[17] Commercialization issues are caused by poor performance in several factors (Figure 2). First, RFBs must use highly concentrated solutions of electrolyte material. As a result, newly designed electrolyte materials must have a solubility that exceeds 2.5 M. However, it has been reported that electrolyte solutions with a concentration that exceeds 0.5 M negatively affects solution viscosity and conductivity.[18] On top of that, electrolytes need to be paired, such that the open-circuit voltage is >1 V in aqueous systems and >2.5 V in non-aqueous systems.[9] Because of these limitations, designing better electrolytes is extremely difficult. Crossover of charged species is also another issue. During battery cycling, charged electrolyte species can permeate through the separator and discharge each other. This crossover event leads to continual capacity loss during battery cycling.[17] Because bulk energy is stored in solution, irreversible capacity loss due to crossover is leads to large energy losses.

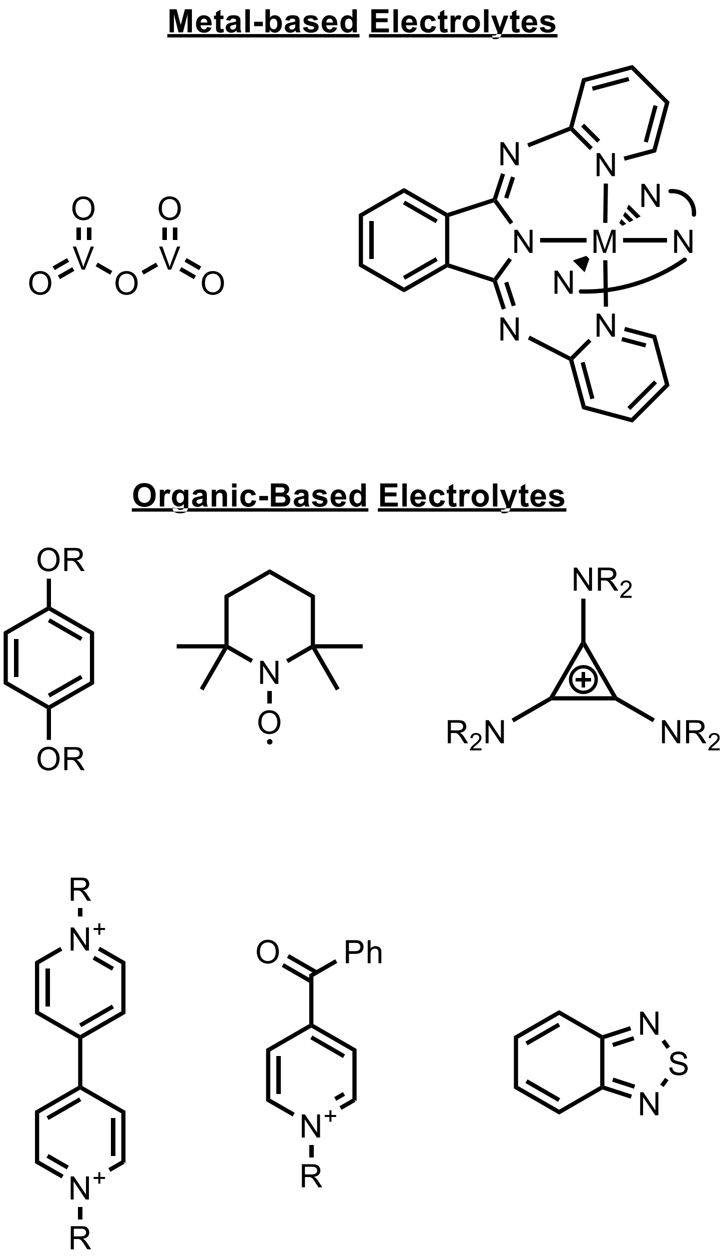

Figure 3: Selected electrolytes for redox-flow batteries.

Many different electrolytes for redox-flow batteries have been synthesized in an attempt to create RFBs that can meet the same battery metrics as Li-based batteries, but at a lower price. Metal-based electrolytes have been used because of their multiple redox states and they generally have higher specific capacity compared to their organic counterparts.[19] The commercial RFB takes advantage of these characteristics by using vanadium-based electrolytes. Skyllas-Kazacos et al. published a vanadium flow battery with high energy density that utilized vanadium oxide electrolytes that was able to reach high electrolyte concentrations greater than 3 M.[20] However, much like the problem with lithium, the global source of vanadium is limited and costs will continue to increase as vanadium is continuously consumed.[13] Utilizing the more abundant transition metals (Fe, Co, Ni, etc.) is a possible solution to the scarcity of vanadium. It was found that the redox properties of a redox-active ligand could be used in RFBs by using metal-ligand complexes as electrolytes. Sanford *et al*. utilized this concept by using bispyridylimino isoindoline ligand (BPI) and a variety of metals as an anolyte material in flow batteries.[21] They tested a variety of first row transition metals and found that the identity of the metal did not affect the redox potential of the complex, which suggested that the redox activity occurs at the ligand, as compared to vanadium electrolytes. However, it was found that the identity of the metal did affect the cycling stability of the complex. It was found that Zn, Mg, and Mn led to irreversible capacity loss during battery cycling, which was attributed to unwanted dissociation of the ligand in the highly coordinating acetonitrile solvent.

One interesting alternative combines Li-ion battery technology and flow battery technology into a redox flow lithium battery.[22–26] The design of this battery utilizes solubilized electrolyte materials to shuttle electrons from the electrochemical cell to solid-state electrode material that is commonly used in Li-ion batteries. Through this design, the high energy density of Li-ion batteries can be achieved in a redox flow battery. Also, the cost benefit of using a redox-flow battery is carried over. Redox flow lithium batteries are able to take advantage of the benefits that arise from Li-ion batteries and RFBs. Unfortunately, this technology is still new and there are a few flaws in the overall design of the material. In order to get efficient charging and discharging of the solid-state material, the redox potentials need to be more extreme than the solid-state material for charging and closer to zero for discharging. This also means that the overall voltaic efficiency of the battery is extremely low. A low voltaic efficiency leads to the energy that was stored at a high voltage can only be accessed at a much lower voltage because of the shuttle design, which follows the principles outlined in the Nernst equation.[23] If the voltaic efficiency problem is addressed by using a shuttle with a redox potential that is the exact same as the solid-state material, the overall utilization of the solid-state material decreases, where the theoretical capacity of the material maximizes at 50% utilization. This was seen in the reported redox-flow lithium batteries where utilization around 30 percent were observed. Combining both Li-ion and redox-flow technology is a relatively new and interesting concept, but more work needs to be done to find a balance between achieving high energy densities with high utilization of storage material and high voltaic efficiencies.

As a completely different alternative to metal-based electrolytes, research has also been focused on using organic-based electrolytes for energy storage in flow battery systems. One of the most common organic electrolyte materials are 1,4-alkoxybenzene derivatives. These catholyte materials have been extensively studied and strides have been made to stabilize some of the issues associated with them. 1,4-alkoxybenzene electrolytes greatly suffer from degradation mechanisms, specifically side reactivity due to the presence of the charged radical species. Studies have found that by increasing the steric bulk around the aryl ring of these electrolyte species side reactivity of the charged species can be suppressed.[27] However, the degradation of these electrolytes are still observed especially due to a dealkylation of the oxygen atoms at the 1 and 4 positions of the arene ring. It was found that this can be slightly suppressed, but the molecular weight of the electrolyte was greatly increased, which in turn vastly decreases its specific capacity. Another popular catholyte species used in RFBs are tetramethylpiperidine oxide (TEMPO) derivatives.[28–30] These derivatives are often highly soluble and their cycling stability is very high. The use of TEMPO derivatives in RFBs have led to many advancements in RFBs, but their low redox potential often limits the overall voltage of the battery. A recent new catholyte species was reported that addressed the low redox potential of catholyte species. Based off cyclopropenium cores, Sanford *et al.*

reported the synthesis of tris(alkylamino)cyclopropenium derivatives that possessed high redox potential, excellent cycling stability, and high solubility in acetonitrile.[31,32]

On the anolyte side of the battery, many of the published electrolytes are often based on aromatic, heterocyclic cores. One of the most common anolyte materials are based off a N,N'-dialkyl-4,4'-bipyridinium core, also known as viologen. Viologen is an excellent electrolyte material and it is very easy to synthetically adjust the electrochemical and physical properties. Viologen has been used as a soluble electrolyte in both the monomeric and polymeric form.[28,30,33,34] Similar to the TEMPO-based electrolytes, viologen suffers from a redox potential, whose absolute value is low. A much more negative anolyte was reported, which were similarly based off of a 4-benzoylpyridinium core. It was found that the pyridinium possess two overall reduction potentials that could drastically increase the amount of energy stored per molecule, thereby increasing the overall capacity of the battery.[35] Also, the 4-benzoylpyridinium core was used in a study that showed a physical organic approach could be used to improve the performance and battery metrics of the electrolyte itself. Computational and experimental work were combined to synthesize an "ideal" version of the 4-benzoylpyridinium anolyte species.[36] This study is extremely important to battery design because it shows that the ability to synthetically tune organic based electrolytes can be used to drastically adjust the performance of electrolytes in RFBs. A much more negative anolyte was also reported with excellent stability, which was based off a benzothiadiazole core.[37] Characteristic of their wine color, these electrolyte species had a redox potential that is one of the most negative of organic flow electrolytes.

Conclusion: Large-scale integration of renewable energy into the electrical grid is of extreme importance due to the environmental damage that is caused by the utilization of fossil fuels.

Unfortunately, current technology is not advanced enough to allow for full integration of renewable energy. While renewable energy sources are slowly being incorporated into the electrical grid, much larger strides need to be taken to increase the rate at which renewable energy is incorporated. Improving EES technology should be a high priority, since efficient storage is required to prevent a destabilized grid that can arise from direct integration of renewable energy into the grid. Of the available technology, Li-ion batteries are the most advanced and "market-ready". However, in order to get global integration of renewable energy and to scale Li-ion batteries to the necessary size for grid-scale storage, production costs and safety are of concern. Many alternatives have been reported recently to address these issues, where inexpensive electrode materials, such as sulfur and sodium, are being used. Recently, redox-flow batteries have garnered a lot of interest as one of the more promising alternatives to Li-ion battery technology because their design is inherently scalable, which leads to the potential for inexpensive, grid-scale batteries. However, low energy density and high costs still preclude most redox-flow batteries from being commercialized. Fortunately, recent research has been done to address these issues with many new electrolytes being designed that can lead much higher energy densities in redox-flow batteries. Also, it has also been shown that redox flow and Li-ion technology can be combined to take advantage of the benefits of both systems to create a new redox-flow lithium battery. However, much more research on improving redox-flow technology still needs to be done to achieve the goals set by the DOE. Fortunately, the future of renewable energy is growing and new technology are being invented to achieve the grid-scale renewable electrical energy.

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