CHAPTER 1

INTRODUCTION: RENEWABLE ENERGY STORAGE

Motivation: The Need for Storage

Progress in generation of carbon-neutral renewable energy has been rapid over the last decade and is projected to grow to meet nearly half of world electricity demand by 2050 (Figure 1).[1] As renewable energy becomes widespread and cost-competitive with fossil fuels, there will be increasing need for efficient, carbon-neutral storage technologies that can operate on a wide variety of time and power scales.

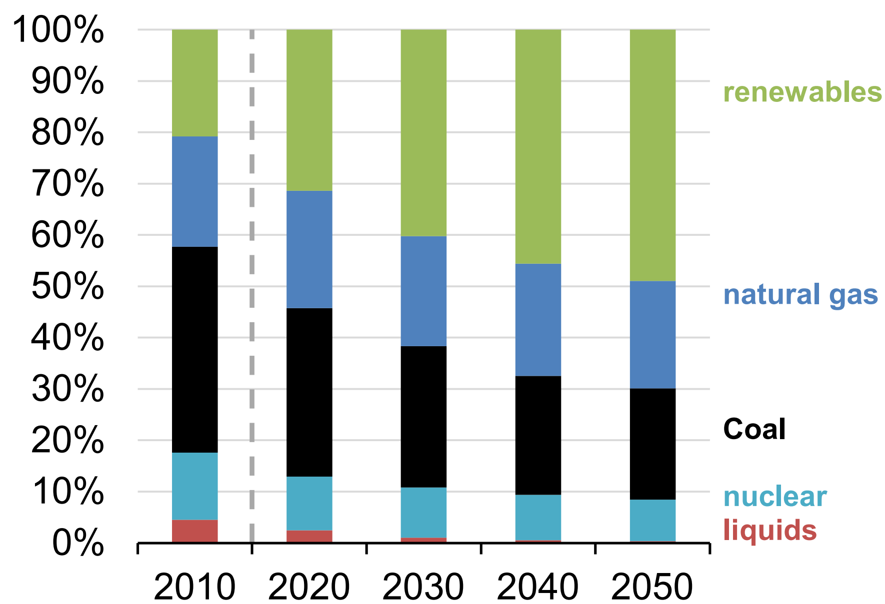

Figure 1: Share of net electricity generation, world. Source: US. Energy Information Administration International Energy Outlook, September 2019 (Public Domain).

The most abundant sources of renewable energy, sunlight and wind, are intermittent and need to be stored at peak production to be used most efficiently. In California, where solar photovoltaics have become ubiquitous, the high production of solar energy has created a problem known as the "duck curve" (Figure 2).[2] The peak of solar production occurs earlier in the day than peak electricity demand, resulting in a sharp rise in the net load on the grid as the sun sets, which requires generators to ramp up production very quickly. As solar gains even higher adoption rates, there will be an increasing number of sunny summer days where peak solar production outstrips demand and will need to be curtailed by grid operators, wasting energy. Wind power also varies on hourly, daily, and seasonal timescales that are uncoupled from demand, creating similar but even less predictable grid balancing and overgeneration problems.[3] The grid-level ability to store energy from these intermittent sources during periods of high production to be used during periods of low production and high demand is key to reducing strain on power plants and electrical grids, lowering the cost of renewable energy, and increasing the penetration of renewables.

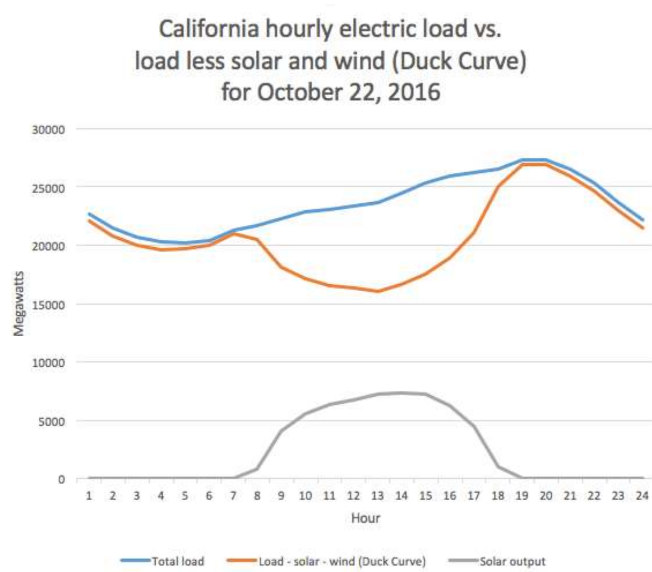

Figure 2: Illustration of the "duck curve". Created by Arnold Reinhold and reproduced under the Creative Commons Attribution-ShareAlike 4.0 International license.

A further challenge in the storage of renewable energy is applications such as long-range transportation and aviation which require energy sources that have a high energy density and fast refueling. These are the applications which are most difficult to transition from fossil fuels, which have high mass and volume energy densities (Figure 3).[4] While there are increasing adoption rates for light duty electric vehicles, especially in large, newly-industrialized countries such as China and India, the Li-ion batteries in those vehicles are too large and costly for heavy-duty applications such as freight transportation.[5]

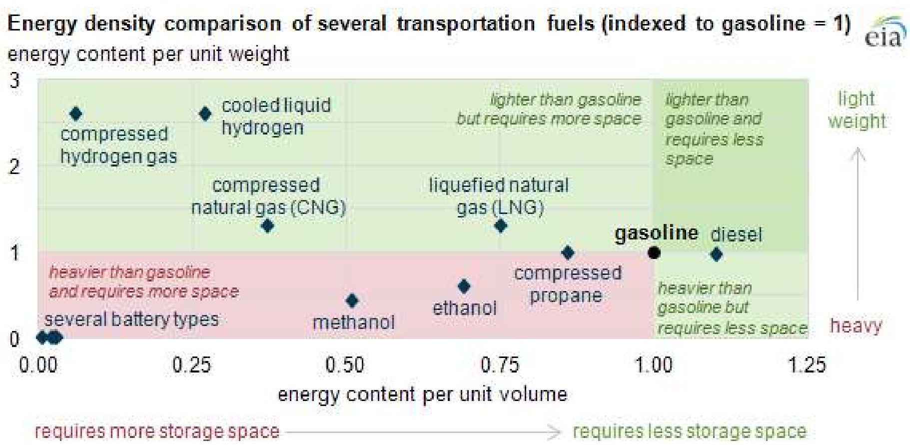

Figure 3: Energy density comparison of transportation fuels. Source: Energy Information Administration (Public Domain).

A wide variety of storage solutions will undoubtedly be needed for different sectors and different applications. Among the most efficient and flexible storage methods is electrochemical energy storage, wherein chemical oxidations and reductions store the energy – in short, batteries.[6] The work in this dissertation represents fundamental science with potential applicability to two types of electrochemical energy storage technologies: hydrogen fuel cells and redox flow batteries.

Hydrogen Evolution, Oxidation, and Fuel Cells

Hydrogen derived from water splitting has been recognized as a key target for energy storage and fuel applications since the oil embargo of the 1970s.[7,8] While the initial interest was in developing alternatives to petroleum in order to secure energy independence from Middle Eastern oil producers, the climate crisis has renewed interest in hydrogen as a carbon-neutral energy source. Additionally, industrial feedstocks of hydrogen are currently primarily derived from steam reformation of hydrocarbons and the water-gas shift reaction, which are not only carbon intensive in their energy demands, but also produce CO_2 as a coproduct.[9] Development of renewable energy-fueled processes for producing hydrogen from water is therefore expected to be a key step toward the decarbonization of the global economy.

Electro- or photoelectrocatalysts for the hydrogen evolution reaction (HER) are frequently targeted for use in the cathode of water electrolyzers, and there has been rapid progress in the development of Earth-abundant catalysts.[10,11] However, a reversible catalyst which is also competent for the hydrogen oxidation reaction (HOR) has the advantage of being useful for water-based fuel cells, which are safer and more efficient than combustion at liberating energy from hydrogen. Hydrogen fuel cell cars additionally have several advantages over battery-powered electric vehicles, as they have longer driving ranges, faster refueling times, and are less disruptive to the electric grid.[5] State-of-the-art commercial electolyzers and fuel cells both currently use Pt or IrO_2 catalysts,[12,13] which are too rare and expensive to be a scalable and economical solution long-term and are a major contributor to the higher cost of hydrogen cars.[5] Thus, it is a critical area of research to identify Earth-abundant catalysts that are competent for HER and HOR to replace them.

Naturally occurring hydrogenases are a typical source of inspiration in this field, since they are reversible and contain only Earth-abundant Fe and Ni.[14] Indeed, a NiFe hydrogenase has been shown to catalyze HOR at a rate comparable to Pt.[15] HOR catalyst development has occurred primarily in the solid-state material realm, but despite success in reducing the Pt loading for proton-exchange membrane (PEM) fuel cells,[13] precious-metal-free catalysts are still unusual.[16] Even less well-studied are Earth-abundant small-molecule catalysts which are capable of reversibly catalyzing the interconversion of protons and electrons with hydrogen.

Redox Flow Batteries

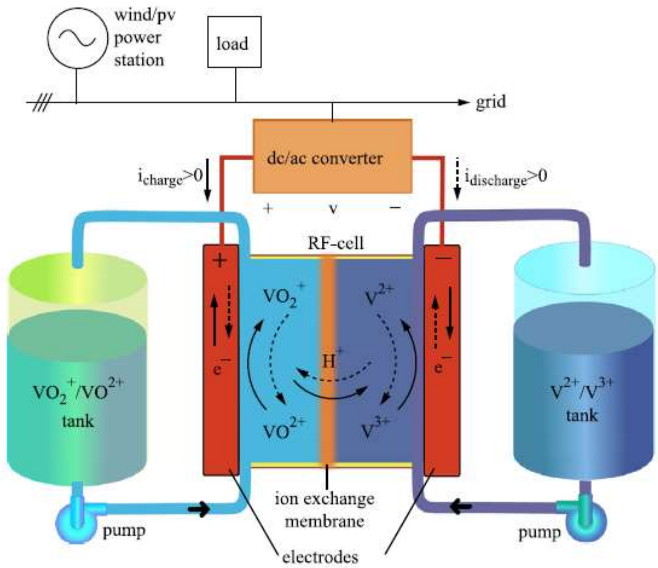

Figure 4: Diagram of a vanadium-based redox flow battery. Reproduced with permission from the copyright holder, Elsevier, from reference 6.

A redox flow battery (Figure 4) uses a solution-phase redox couple to store energy, as opposed to the solution-to-solid phase couples used by most conventional batteries. As the battery is charged, the charged electrolyte is pumped into a storage tank, and pumped back to the electrodes during discharge. Although it results in a low energy density, this design is advantageous for large, stationary applications such as grid balancing, since the capacity of the flow battery is as large as the storage tanks.[6,17] Additionally, unlike hydrogen fuel cells, redox flow batteries have no need for catalysts to assist the charge and discharge process, as the transfer electrons directly with the electrode.

A current limitation in redox flow battery technology is the reliance on water as the solvent. Water has an electrochemical stability window of only 1.23 V, limiting the cell voltage, and a high freezing point relative to outdoor temperatures during winter in much of the world. Non-aqueous redox flow battery electrolytes are desirable for applications where higher voltages or lower working temperatures are needed, as there are many organic solvents which can overcome these limitations.[18]

In order to be a good candidate electrolyte for nonaqueous redox flow batteries, a molecule must have several properties. First, it must have a reversible electrochemical couple in the stability window of the desired solvent. Second, it must be stable in both the charged and discharged states over a long period of time and many charge/discharge cycles. Third, it should have high solubility in the solvent, which will improve the energy density of the battery.

The difference in voltage between the reduction potentials of the two couples employed sets the maximum cell voltage. If the same molecule has two suitable couples, it can be used to make a symmetric redox flow battery, which confers additional stability to the system in the event of membrane crossover over time.[19]

Summary of this Dissertation

Chapter Two of this dissertation focuses on one member of a series of macrocyclic Co catalysts that have been extensively studied for HER and its reaction with hydrogen. Further mechanistic information in this field is expected to aid the development of Earth-abundant catalysts for HER and HOR.

Chapter Three of this dissertation describes the synthesis and boronation of a new Ru bipyridine cyanide complex. This work aimed to improve on previous work toward developing symmetric nonaqueous redox flow battery electrolytes using similar molecules.

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