Chapter 1

INTRODUCTION: GLOBAL WARMING, ENERGY AND ARTIFICIAL PHOTOSYNTHESIS

Though I cannot recall exactly when and what piqued my interest in global climate change and energy systems, by my senior year of high school my fascination was advanced enough that one of my Stanford undergraduate application essays focused on the (then) recent developments and improvements in hydrogen fuel vehicles. I remember thinking then (as I do now) that moving to vehicles that only emitted water from their exhaust pipes would be truly transformational. Thus it surprised no one that by my sophomore year of college I had joined the newly established lab of Professor Thomas Jaramillo and started investigating novel protection layers for photoelectrochemical water splitting devices. This interest in solar driven chemical syntheses would follow me throughout my time at both Stanford and Caltech and has included explorations into many different aspects of such systems including light absorbers, catalysts, systems integration, and their economic viability. Now, nearly a decade later, though I have a much broader, nuanced, and perhaps more pessimistic understanding of the energy ecosystem, I remain just as committed to working on finding new and disruptive ways to change it. This introductory chapter serves as a short primer on the current state of energy production, global warming, and photoelectrochemical cells.

1.1 Energy and the Climate

1.1.1 Global Energy Consumption

In the past several decades, global energy consumption has increased tremendously, more than doubling since 1971 (Figure 1.1) reaching ~14000 millions of tonnes of oil equivalent (Mtoe) in 2014. Though the amount of energy consumed has increased markedly, our main energy sources have remained remarkably consistent with over 80% of our energy coming solely from three fossil-fuel sources (oil, natural gas, and coal). Electricity production shows a similar trend with electricity generation increasing almost six fold since 1971 with the main source remaining fossil fuels (Figure 1.2).[1]

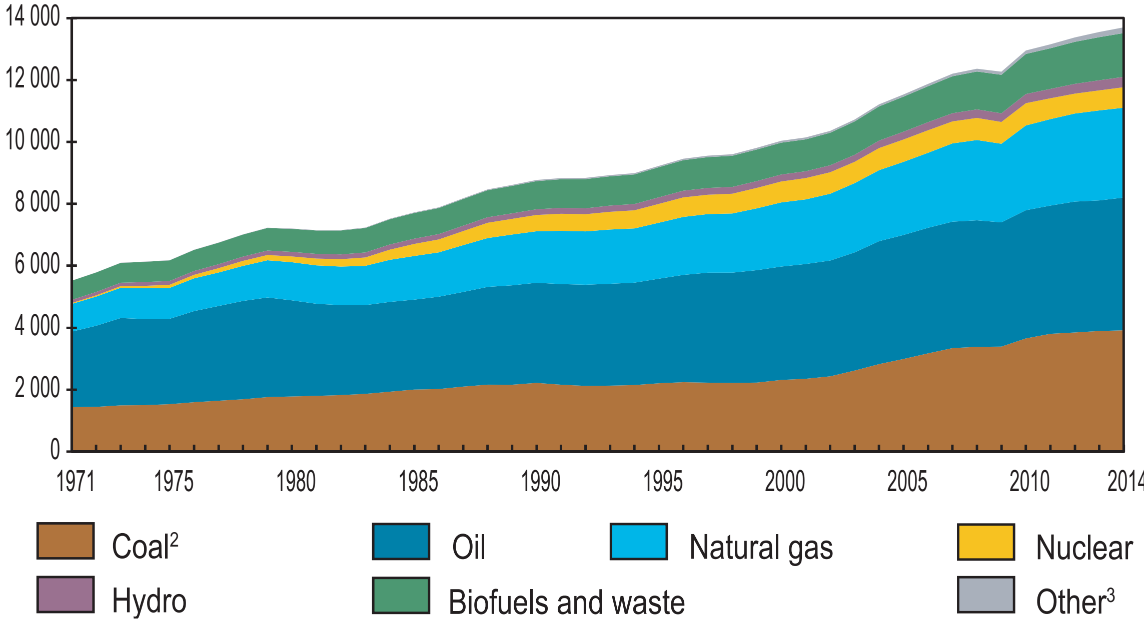

Figure 1.1: World total primary energy supply (TPES) from 1971 to 2014 by fuel (Mtoe).[1] © OECD/IEA 2016 Key World Statistics, IEA Publishing. License: www.iea.org/t&c

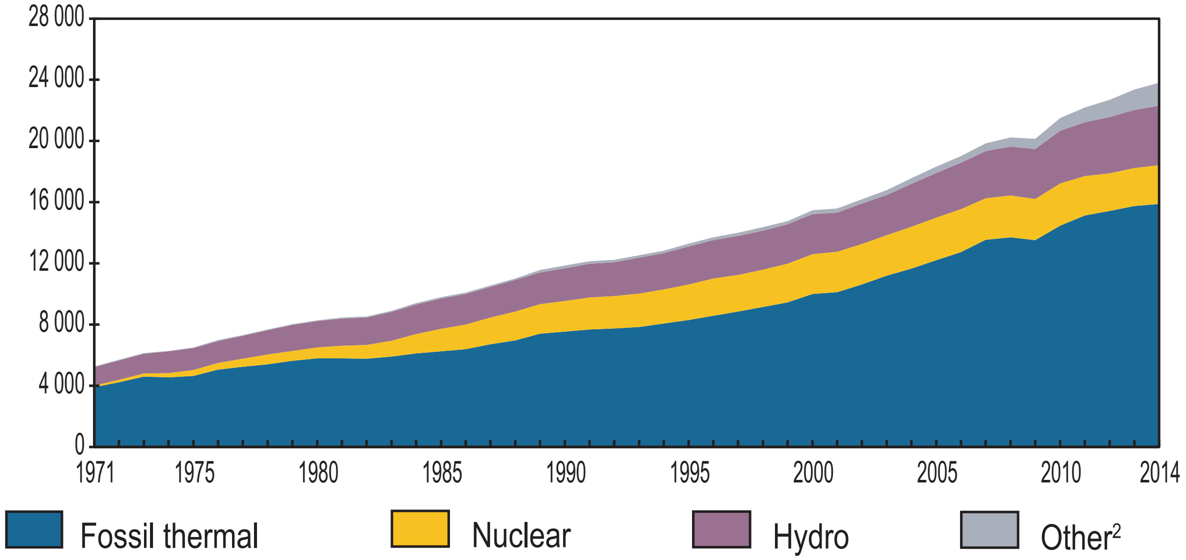

Figure 1.2: World electricity generation from 1971 to 2014 by fuel (TWh).[1] © OECD/IEA 2016 Key World Statistics, IEA Publishing. License: www.iea.org/t&c

Furthermore, global energy consumption is expected to continue rising in the future reaching ~21000 Mtoe by 2050.[2] This increase in energy consumption has been coupled with tremendous global economic growth, with global GDP per capita increasing ten-fold from $866 in 1971 to over $10,000 in 2014 (inflation adjusted).[3] Unfortunately, while this increase in energy consumption, particularly in developing nations, has come with several benefits, the burning fossil fuels also leads to the direct emission of carbon dioxide and other pollutants into the atmosphere. These pollutants, including NO_x and SO_x, have been shown to adversely affect the environment and global ecosystem causing effects such as acid rain and smog.[4] With total energy consumption expected to rise, decisions about where we obtain our energy will be ever more important.

1.1.2 Carbon Dioxide Emission

Since 1971, the amount of anthropogenic carbon dioxide emitted globally has more than doubled (Figure 1.3). This increase in global carbon dioxide emission is largely due to the increase in fossil fuel combustion, which accounts for ~80% of anthropogenic carbon dioxide emission.[5]

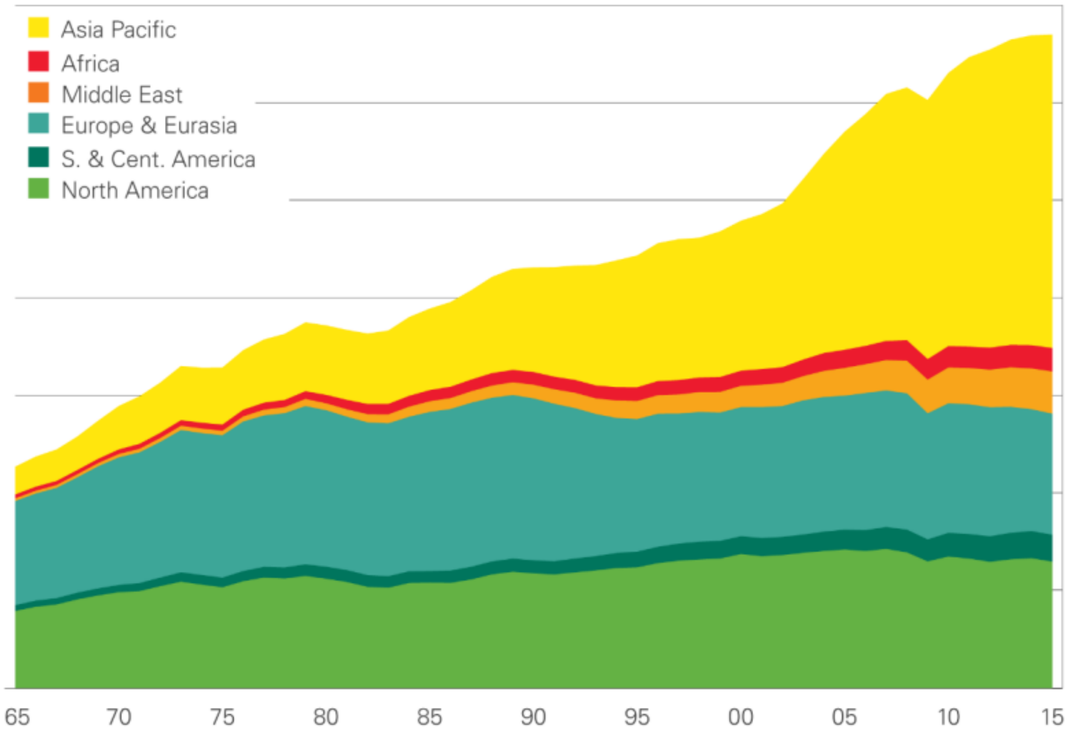

Figure 1.3: Annual global carbon dioxide emissions from 1965 to 2014 (million tonnes CO2).[6]

It is estimated that approximately 60% of anthropogenic emission of carbon dioxide is released into the atmosphere with the majority of the rest being absorbed by oceans.[7] While anthropogenic carbon emissions are relatively small compared to the overall magnitude of the carbon cycle, their net effect has been quite significant. The anthropogenic carbon dioxide absorbed by the oceans has led to an ocean acidification of ~0.1 pH and significant damage to the health of marine ecosystems, in particular to coral reef health.[8] Additionally, the level of carbon dioxide in the atmosphere has increased rapidly from 320 ppm in 1960 to over 400 ppm by 2014 (Figure 1.4), a rate hitherto unobserved.

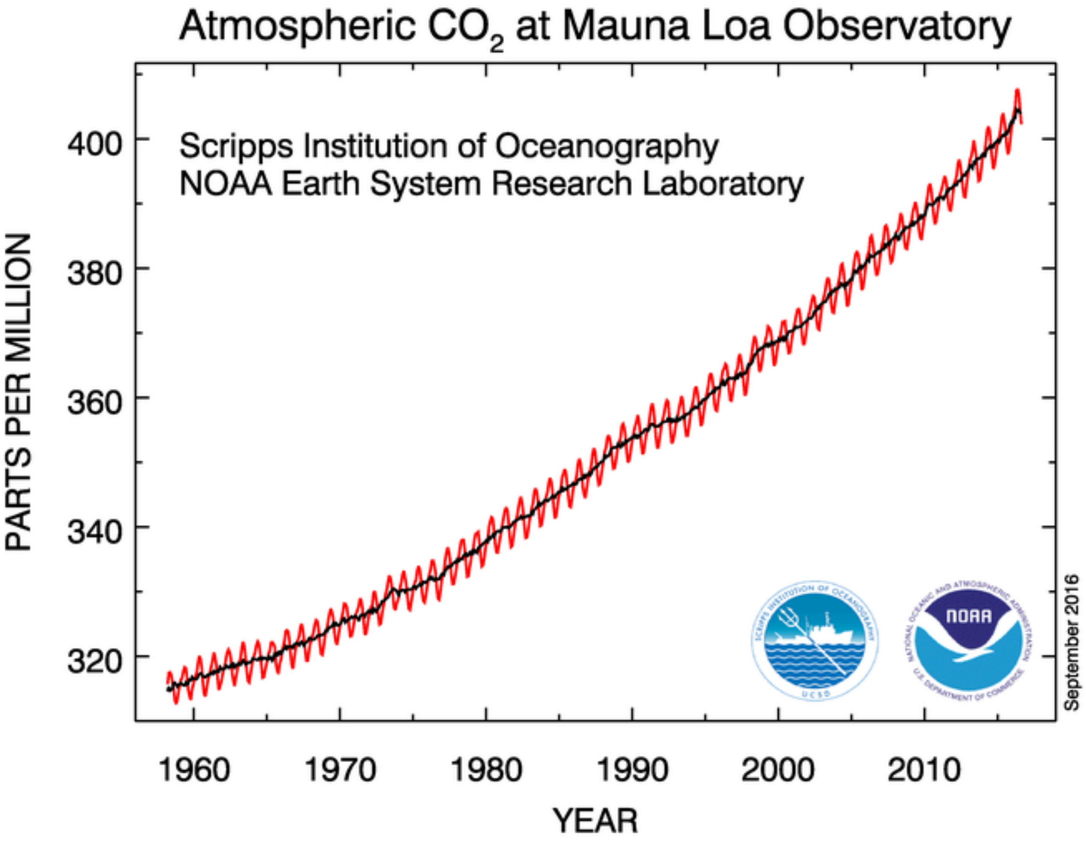

Figure 1.4: Monthly mean atmospheric carbon dioxide at Mauna Loa Observatory, Hawaii. Publically available from NOAA.[9]

1.1.3 Global Climate Change

Over the past fifty years, there has been a clear increase in both land and ocean average surface temperature (Figure 1.5). The increase in atmospheric carbon dioxide, as well as light hydrocarbons, is believed to contribute significantly to this increase in temperature through a process commonly known as the greenhouse effect. Though often considered controversial, it is estimated that 97% of climate change scientists believe in anthropogenic global warming.[10]

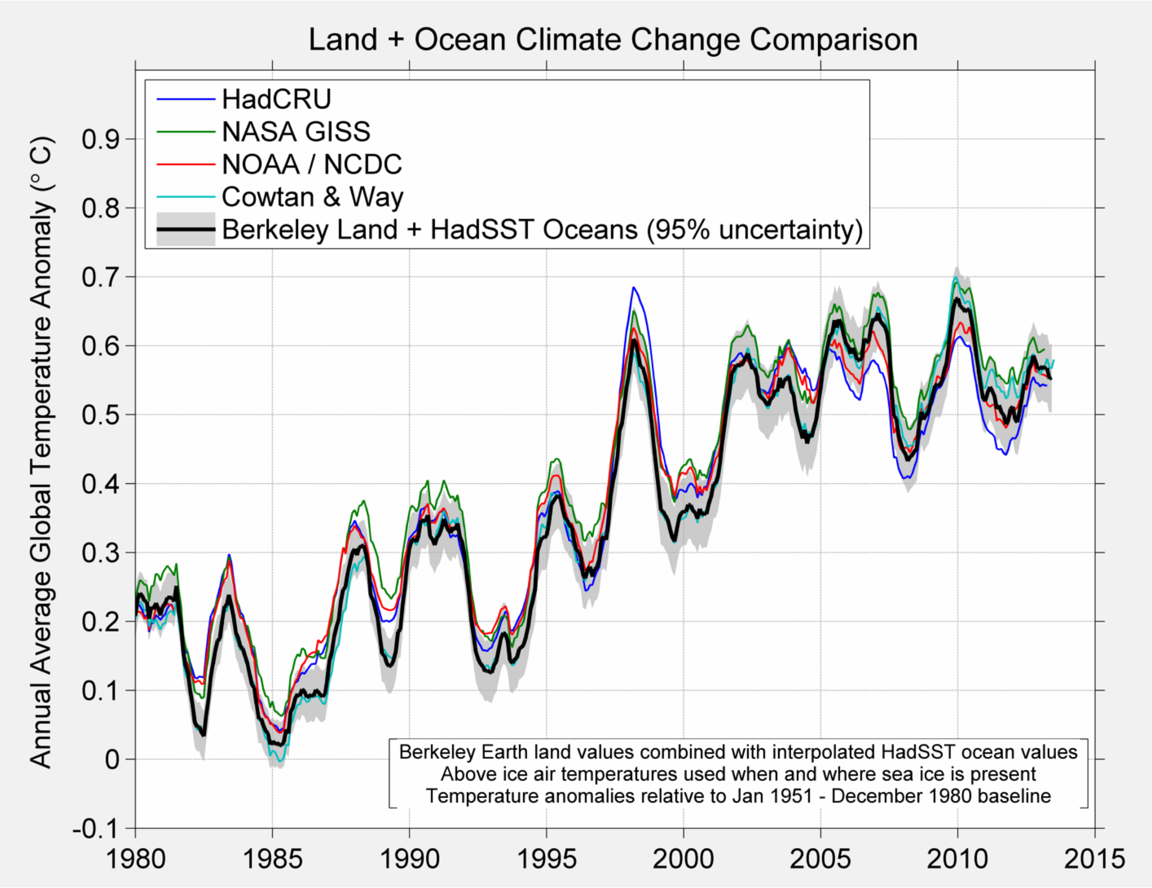

Figure 1.5: Anomalies of the global temperature index of provided by several groups is depicted for the 1980 to present time period. The base period is 1951-1980. The Berkeley baseline is depicted. Publically available from the BEST report.[11]

While there are many studies that attempt to estimate future effects of anthropogenic carbon emissions, evaluating climate models goes beyond the scope of this introduction. Instead I will simply assert that we have already managed to increase atmospheric CO_2 and decrease ocean acidity to levels unseen for hundreds of thousands of years.[8]

1.2 Breaking the Energy & CO_2 Emission Bond

So far in this chapter we have seen that increased energy use has led to both improved economic prosperity as well as increased anthropogenic carbon emissions. These emissions have been shown to cause significant and lasting effects to our environment and health. That is the global emissions problem that we are currently facing. The only way to break this pattern is by decoupling energy consumption and carbon emissions. This can be done by two main ways: shifting to energy sources that are carbon-neutral or sequestering the carbon dioxide so that it does not escape into the atmosphere or bleed into the oceans. While there are many different energy sources that can be used in lieu of fossil fuels, several of these energy sources can only supply a small fraction of total energy needed. In the proceeding sections we will look into some of the more abundant sources of alternative energy and assess their future potential focusing primarily on the main scope of this thesis, photoelectrochemical water splitting.

1.2.1 Carbon Capture and Storage (CCS)

Carbon capture and storage is a process in which carbon dioxide, generated from a large waste source (usually a power plant or cement plant), is captured and stored underground where it cannot escape into the atmosphere. While not all anthropogenic carbon can be captured that way, this would allow us to continue using fossil fuels without increasing carbon dioxide emissions. While it has proven difficult to estimate the cost of

CCS, the U.S. Congressional Budget Office (CBO) has projected that the levelized cost of electricity produced from a supercritical pulverized coal plant would increase by ~70-80% if CCS is implemented.[12] Such high costs for CCS make it very difficult for it to be economically competitive in today's energy climate. Recently several proposed CCS projects such as the FutureGen 2.0 project in Meredosia, Illinois, the Hydrogen Energy California Project in Bakersfield, California and the Texas Clean Energy Project in Penwell, Texas have either been cancelled or put on indefinite hold. It remains to be seen if cost cutting measures and technological innovations will be able to make CCS competitive.

1.2.2 Hydropower

Currently hydropower is the largest alternative energy source accounting for ~16% of global electricity generation (Figure 1.6).[1] It currently supplies over 3000 TWh of electricity annually and has a technical potential estimated to be ~16000 TWh/yr.[13]

There are several benefits for hydroelectricity including its low cost (levelized cost of electricity for hydropower is estimated between 0.05 and 0.1 \$/kWh) as well as the ability to use hydro plants a cheap ways to store energy.[14] Unfortunately, hydroelectricity is geographically unevenly disturbed preventing certain countries from being able to utilize it significantly. Additionally, the total hydro capacity, while not insignificant, would only be able to supply ~15% of total energy demanded in 2015 and, seeing as energy consumption is expected to grow significantly in the next few decades, would constitute an even smaller potential share of the energy market in the future. Thus while hydropower will almost certainly play a crucial role in the future, the majority of energy will need to be supplied from other sources.

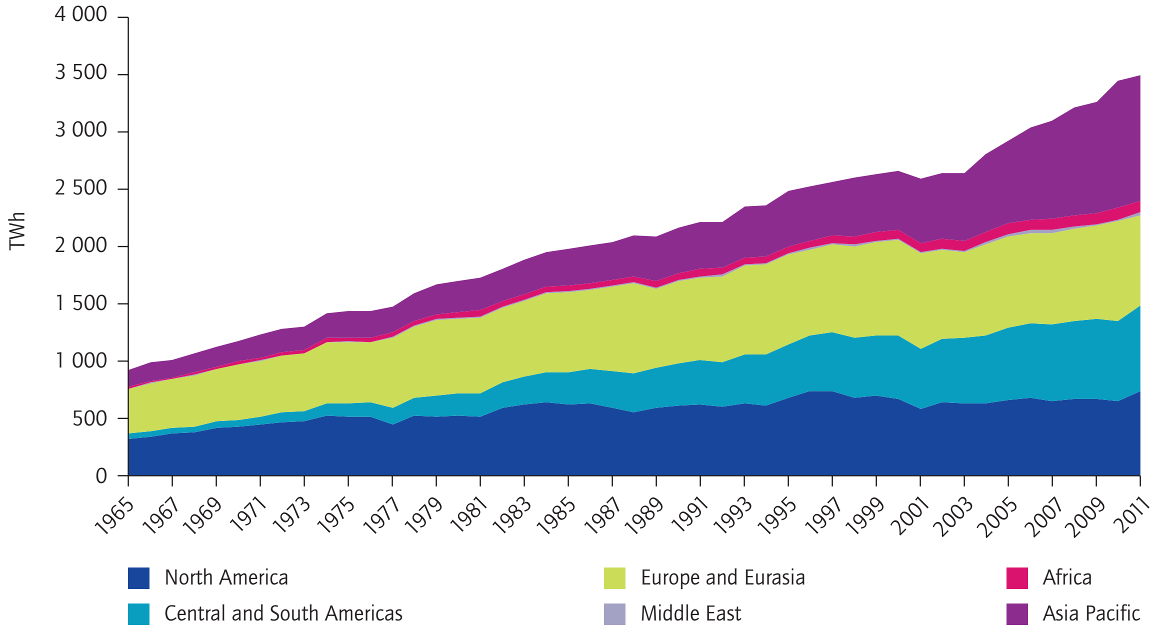

Figure 1.6: Hydroelectricity generation in TWh from 1965-2011.[13]

1.2.3 Nuclear Fission

Though there are many different types of nuclear power plants, they all work by harnessing the thermal energy generated from nuclear fission reactions of fissile material. Nuclear fission is the fifth most commonly used energy source and accounts for ~10% of global electricity generation (~2600 TWh).[6] The levelized cost of electricity from new capacity nuclear is ~0.1 $/kWh.[15]

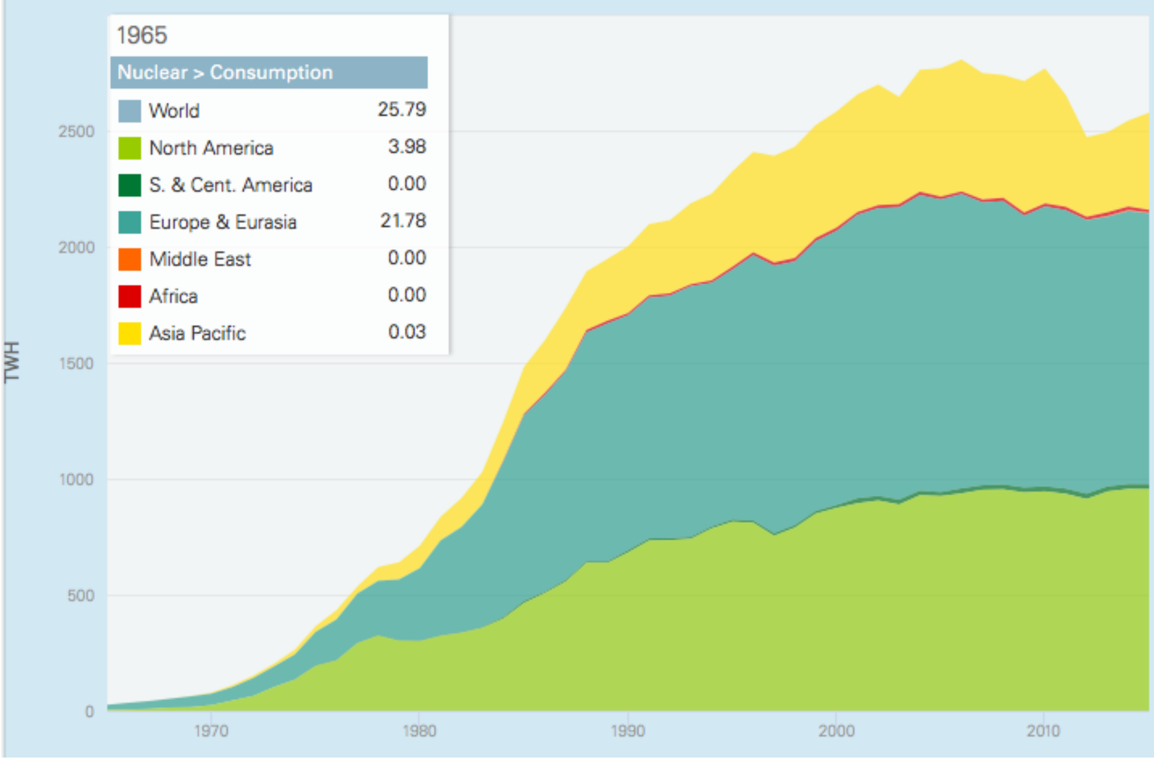

Figure 1.7: Nuclear energy generation from 1965-2014 (Terrawatt-hours).[6]

While nuclear has certain advantages, such as higher capacity factors, compared to many other carbon-neutral energy sources, the growth of nuclear energy has been essentially stalled since 1996.[6] For nuclear fission to remain a prominent part of our energy economy, new power plants will need to be constructed at a much faster rate[2] especially as ~50% of all reactors are over 30 years old and will likely be decommissioned in the next two decades.

1.2.4 Wind Power

The most common way wind power is harnessed is by using airflow to mechanically power large turbines and generate electricity. Encouragingly, the total amount of wind potential has been calculated to be large enough for a significant amount of global energy to be derived from it.[16] Since 2006, the amount of installed wind generation capacity has grown five-fold and is now approximately 435 GW and an annual energy generation of ~841 TWh.[6] Additionally, the levelized cost of wind electricity has decreased significantly in the past three decades with current analyses estimating the cost at significantly less than 0.10 $/kWh for onshore wind and ~0.15 $/kWh for offshore wind.[15]

1.2.5 Photovoltaic Cells

While quite diffuse, the largest available energy resource is sunlight with more solar energy striking the earth in 90 minutes than the total energy consumed in 2015.[2] Photovoltaic cells directly convert solar energy into electricity by harnessing the electrical potential in semiconductor junctions. While there are several semiconducting materials that can be used in solar panels including CIGS, CdTe, GaAs, and perovskites, silicon-based photovoltaics accounted for ~90% of total photovoltaic production in 2013.[17] By 2015, over 200 GW of photovoltaics had been deployed globally and capital costs had fallen to ~2 $/W[17] with levelized costs lower than 0.1 $/kWh for utility scale photovoltaics.[15] While photovoltaic capacity has grown rapidly in the past decade, from ~5 GW in 2005 to over 200 GW in 2015, it still accounts for less than 1% of global electricity generation.[6]

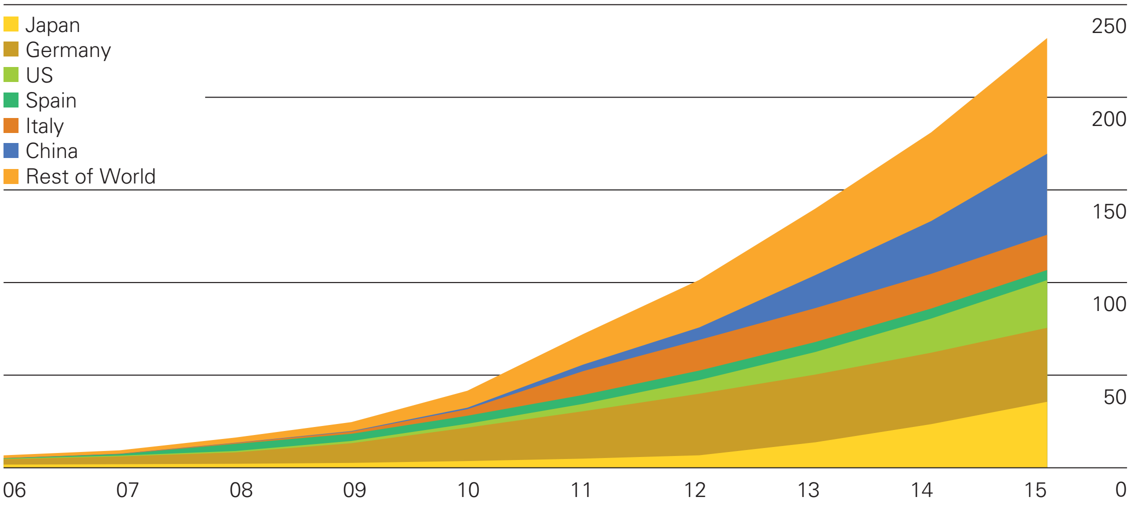

Figure 1.8: Global solar photovoltaic generation capacity (GW).[6]

1.2.6 Concentrated Solar Thermal

Solar thermal is another way to harness solar energy. Solar thermal plants use mirrors or lenses to concentrate solar energy onto a small area and convert it to heat. The four main types of concentrators are parabolic trough collectors, linear Fresnel reflectors, power towers, and dish-engine systems.[17] The concentrated solar energy is converted to heat in either an oil or molten salt and is subsequently transferred to steam that is used to drive an engine and generate electricity. By 2014, less than 5 GW of concentrated solar power had been deployed globally making its market share significantly smaller than that of photovoltaics.[17]

1.3 Artificial Photosynthesis

As previously mentioned, the levelized costs of electricity from wind turbines and photovoltaics are quite low and can even, at times, undercut those of fossil fuels. Given that fact, one may wonder why governments, eager for energy independence, are not investing massive amount of money into solar and wind. The answer lies in these technologies' intermittent nature. The inability to run photovoltaics at night or wind turbines when it is not windy means that if a significant amount of the energy supply comes from those sources, energy storage in cheap and efficient ways is necessary. While there are several different technologies available for energy storage including pumped hydro, compressed air, and several different types of batteries, currently none of them have enough capacity and are cheap enough for them to be viable on a commercial scale.[14]

Artificial photosynthesis is an alternative method to harness solar energy, one which converts solar energy directly into a chemical fuel. Converting solar energy to chemical fuels instead of to electricity has several advantages including lower cost of energy transportation (see Chapter 6), higher energy density allowing for use in transportation vehicles that cannot be electrified and, for certain fuels, the ability to be integrated into existing infrastructure. Additionally, in contrast with photosynthetic organisms which have a yearly efficiency of <1%[18], artificial photosynthetic devices are theoretically capable of much higher efficiencies.[19]

One of the simplest artificial photosynthetic devices is a photoelectrochemical water splitting device in which solar energy is used to split water into hydrogen and oxygen. Though studied for many years, no commercially viable photoelectrochemical device has been developed. This is partially due to the fact that such a device requires the optimization and integration of several different components including the light absorbing materials in which convert the solar energy into excited electron-hole pairs, the membranes which separate the oxygen and hydrogen gases, and the catalysts. For a more in-depth description of photoelectrochemical systems, I refer the reader to recent reviews published by the Lewis group.[20, 21]

Although the free-energy change required to split one molecule of water corresponds to $E^0 = 1.23$ V per electron transferred, the electrolysis of water typically requires the application of an overpotential to drive the kinetically rate-liming steps involved with the multistep oxidation and reduction half-reactions. Catalysts can improve the kinetics and efficiencies of the cathodic (hydrogen-evolution reaction, HER) and anodic (oxygen-evolution reaction, OER) half-reactions. While I have collaborated on several projects during my time at Caltech, my primarily focus was on synthesizing and characterizing new acid stable catalysts for the hydrogen evolution reaction.

When I started, and even to this day, the most efficient water-splitting catalysts contain scarce metals like platinum (for the HER)[20, 22-25] and iridium (for the OER).[20] For photoelectrochemical water splitting to be commercially viable in the terawatt scale, the HER and OER catalysts used in such a system must be made from earth-abundant elements.

Previously, the catalysis of the HER has been demonstrated using materials made from earth-abundant elements such as nickel alloys.[26-30] In particular, nickel-molybdenum alloys require the application of only ~50 mV of overpotential to catalyze the HER at a current density of -10 mA cm^{-2}.[27-33] However, nickel-molybdenum alloys are unstable in strongly acidic solutions,[27, 34] where proton-exchange membranes are operational and where the voltage loss due to the formation of a pH gradient across the membrane can be minimized.[34, 35]

This thesis will focus on the work I have done to synthesize and characterize new acid stable hydrogen evolution catalysts. When I first joined the Lewis group, molybdenum disulfide had recently been reported as an acid stable HER catalyst. In consultation with Nate, my first project focused on expanding our understanding of the catalytic activity of related group VI chalcogenides, primarily molybdenum diselenide. I then collaborated with Azhar Carim on assessing the activity of another chalcogenide, cobalt selenide. Though these catalysts were found to be quite promising, the transition metal phosphide family, first characterized by the Schaak and Lewis groups, showed even greater potential. Intrigued by these new catalysts, I devised a new method to electrodeposit transition metal phosphides and decided to focus my efforts on understanding their *operando* chemical composition. In addition to that work, I have also included a chapter on the cost of energy transportation via different fuels, which was work that originated during my fellowship at the Dow Centre for Sustainable Innovation and was done to get a better sense of the economic feasibility of future energy transportation landscapes.

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