

An Exploration of Titanium Oxide Hydrate/Polyalcohol Hybrids for Solar Energy Harvesting and Storage

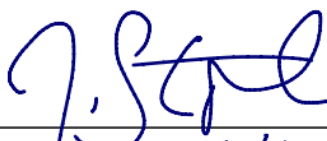
A Thesis

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1. Introduction

Global energy consumption is projected to double by 2050 compared to 2022 energy needs (1). Meeting growing energy demands while addressing carbon neutrality targets will require more efficient and more versatile technologies for renewable energy generation and storage. Photo-rechargeable batteries are a promising technology to achieve this goal because they integrate renewable energy harvesting and storage capabilities into a single device. Their combined design overcomes the primary drawback of solar power: the intermittent availability of the sun. One photo-rechargeable battery design is a redox flow battery, where solar energy is stored via photochemically-active redox couples within liquid electrolytes (2). Photo-rechargeable redox flow batteries have been designed with entirely inorganic electrolytes, such as a system of aqueous I^-/I_3^- , or entirely organic electrolytes, such as aqueous quinoxaline derivatives (3). However, these electrolytes are limited in their ability to store energy for extended periods of time.

This energy storage challenge can be solved by combining inorganic and organic species into a hybrid material. Particularly interesting materials for photo-rechargeable battery fuels are inorganic/organic hybrid solutions of titanium oxide hydrate and a polyalcohol. Prior research has illustrated that, when illuminated with UV light, titanium oxide hydrates photoreduce from the +IV to the +III oxidation state (4). An electrical current can then be generated in the reverse reaction, which is relevant for energy storage. The addition of a polyalcohol improves the stability of titanium oxide hydrates and broadens their applications. It is proposed that the polyalcohol chelates to the titanium oxide hydrate complex, reducing precipitation

of the hydrate as titanium dioxide (TiO_2) as well as heightening stability of titanium(III). Consequently, photo-rechargeable redox flow battery electrolytes developed from these hybrids would have longer lifetimes and more efficient energy storage than neat titanium oxide hydrates. However, the role of the polyalcohol within titanium's photoreduction is not well understood and could explain the properties of the formed hybrid material. This research aims to elucidate the photoreactions within titanium oxide hydrate/ polyalcohol hybrids to advance our understanding of these versatile materials systems, particularly for solar energy harvesting and storage.

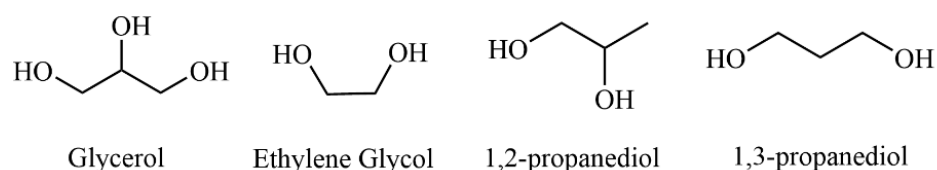


Figure 1.1 Polyalcohol Structures. Four polyalcohols with differing location and density of hydroxyl groups will be considered in the proposed research.

To achieve this goal, the organic species in titanium oxide hydrate/glycerol hybrids with and without UV illumination will be characterized to propose a photoreduction mechanism. Then, the optical and electrochemical properties of hybrids prepared with titanium oxide hydrate and various polyalcohol will be explored with spectroscopy and electrochemistry techniques. Comparing the properties of hybrids prepared with different polyalcohol will assist in identifying relevant interactions between titanium oxide hydrate and the polyalcohol. Delivering a mechanistic understanding of polyalcohol hybrids and their applications will help advance the energy storage capabilities of solar energy technologies, specifically photo-rechargeable redox flow batteries. This will

encourage the use of renewable energy technologies to sustainably meet global energy needs, benefiting energy consumers because they would have a more accessible energy source without furthering environmental damage.

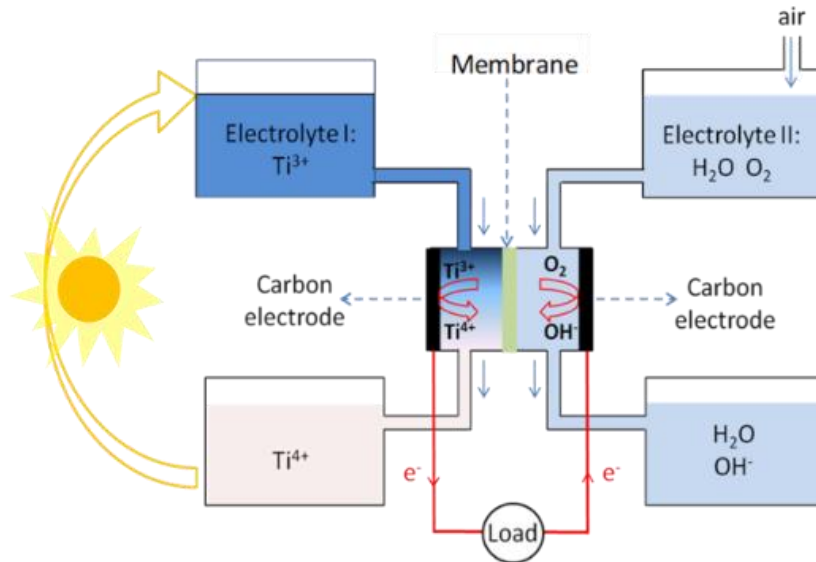


Figure 1.2 Titanium Oxide Hydrate Hybrid Photo-rechargeable Redox Flow Battery. Schematic of a photo-rechargeable redox flow battery utilizing a titanium oxide hydrate hybrid as an electrolyte.

2. Literature Review

Titanium oxide hydrate/polyalcohol hybrids fit within the classification of an inorganic/organic hybrid material, herein referred to as hybrids, because they consist of inorganic and organic components. The current body of research has explored hybrids of titanium oxide hydrates and poly(vinyl alcohol) (PVA) or glycerol, illustrating that the addition of the organic can significantly increase the applications of titanium oxide hydrates (4). Hybrids based on titanium oxide hydrate and polyalcohols other than glycerol have not been explicitly investigated, and besides comparison to other hybrid systems, their interactions are largely unknown. Similarly, the photoreactions within these hybrid materials have yet to be defined. Here, the properties of titanium oxide hydrates, the stability of titanium oxide hydrate/polyalcohol hybrids, and applications of these hybrids for solar energy harvesting and storage will be discussed to frame the research within this thesis.

2.1 Properties of Titanium Oxide Hydrates

Titanium oxide hydrates have the general chemical structure $Ti_xO_y(OH)_z(H_2O)_v$, and are primarily used as intermediates to synthesize titanium dioxide powder from precursors like titanium tetrachloride ($TiCl_4$) (4). Other applications of neat titanium oxide hydrates are limited because of the high instability of these complexes. Aging, the addition of bases, or heat, can cause the precipitation of titanium oxide hydrates into amorphous titanium dioxide, which has

no value for applications beyond titanium dioxide power synthesis (5). The advantage of using titanium oxide hydrates for applications besides titanium dioxide synthesis is their low cost, the ease to produce them in a liquid and solid state, and the large number of precursors that can be used to produce them. Regardless of these benefits, the challenge of preventing neat titanium oxide hydrate precipitation has deterred the study of these hydrates.



Figure 2.1.1 Titanium Oxide Hydrate Photochromism. The photochromic response of titanium oxide hydrate/glycerol hybrids is visible by eye and depends on the species of titanium oxide hydrate, mononuclear (i) or polynuclear (ii), and unirradiated (top) or irradiated (bottom) (6).

In 2010, Russo *et al.* demonstrated that titanium oxide hydrate/glycerol hybrids had a photochromic response to UV light, turning them from transparent to blue. This response results from the photoreduction of titanium from the +IV to the +III oxidation state (6). Photochromism due to redox reactions has been reported for other metal oxides, such as nanocomposites containing phosphomolybdic acid ($H_3PMo_{12}O_{12}$) or phosphotungstic acid ($H_3PW_{12}O_{12}$) (7). Characterizing hybrid photochromism provided a method of exploring the photoreduction of titanium, and metal oxides in general. Ultimately, this opened a pathway of applying titanium oxide hydrate/glycerol hybrids towards energy

storage via reduction and energy production via oxidation, which is the basis of a hybrid solar fuel that can generate, store, and release energy.

2.2 Hybrid Stability

The stability of titanium oxide hydrate/glycerol hybrids is higher than the stability of neat titanium oxide hydrates, promising broader uses of these hybrids. According to Russo *et al.*, glycerol hybrids remain transparent upon mixing as titanium dioxide precipitation is prevented for a minimum of several weeks at room temperature (4). In strong contrast, neat titanium oxide hydrates precipitate into titanium dioxide within hours at room temperature. Although Russo *et al.* thoroughly described the photochromic properties of titanium oxide hydrate/glycerol hybrids, their electrochemical properties, such as the voltage generated with UV illumination, were not detailed. Additionally, these authors only focused on hybrids of titanium oxide hydrate and glycerol. Elucidation of the photochromic and electrochemical properties of hybrids produced from different polyalcohols may provide a more detailed understanding of how the location of alcohol groups influences photochromic as well as electrochemical properties.

Hybrid stability has been more rigorously investigated in hybrids of titanium oxide hydrate and hydroxy carboxylic acids, e.g., citric acid. By crystalizing these hybrids and determining their structure with X-Ray diffraction, it was illustrated that hydroxy carboxylic acids chelated to the titanium oxide hydrate complex (8). The hybrid's high stability, resulting from chelation, can be explained with the Partial

Charge Model. A multidentate ligand binds with a greater affinity to titanium, or metal complex in general, decreasing its partial positive charge and preventing the polycondensation and subsequent precipitation of that complex (9). Given the high stability of titanium oxide hydrate/glycerol hybrids, chelation between glycerol and the titanium oxide hydrate complex is expected.

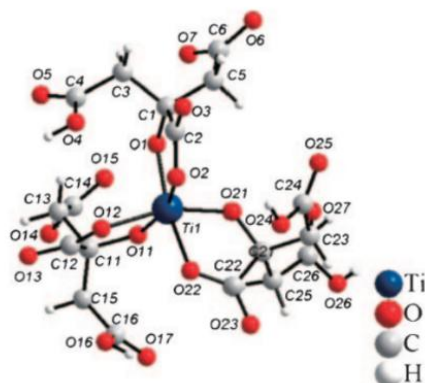


Figure 2.2.1 Mononuclear Citro Titanium Complex Structure. With X-ray diffraction, it was shown that citric acid chelates to titanium and that more than one citric acid molecule coordinates to the titanium complex (8).

The work of Torgunrud *et al.* further supports the likelihood that chelating interactions exist within titanium oxide hydrate/polyalcohol hybrids. They concluded that silica depolymerization with monoalcohols was thermodynamically unfavorable, but the depolymerization could be favorable with polyalcohols (10). Because polyalcohols chelate to silicon and monoalcohols do not, this demonstrates the positive effect of chelation on product stability. One limitation of this work is that it was performed with silicon, not titanium, so direct comparisons between the systems may be limited. However, this work provides strong evidence that chelating is highly favorable, a useful insight for titanium oxide hydrate/polyalcohol hybrids.

Kakahana *et al.* also demonstrated that hydroxy carboxylic acids that formed five-membered rings when chelated to titanium resulted in more stable hybrids than those that formed four or six membered rings (8). Although this was determined qualitatively by comparing the transparency of hybrids over time, the higher stability of five-membered rings have been demonstrated elsewhere. Products of alkylorthosilicate metathesis of silicic acid with five-membered ring ligands had a higher percent conversion than products with six-membered ring ligands, indicating the former was more stable (10).

Alternatively, it has been proposed that six-membered ring interactions with titanium oxide hydrates are more stable. The hypothesis is that PVA forms a six-membered ring with titanium oxide hydrate (11). The high transparency of titanium oxide hydrate and PVA hybrid films, demonstrating that the polymer matrix can effectively prevent condensation of titanium oxide hydrates into particles less than 10 nm in diameter, supports the position that a six-membered ring is favored (12).

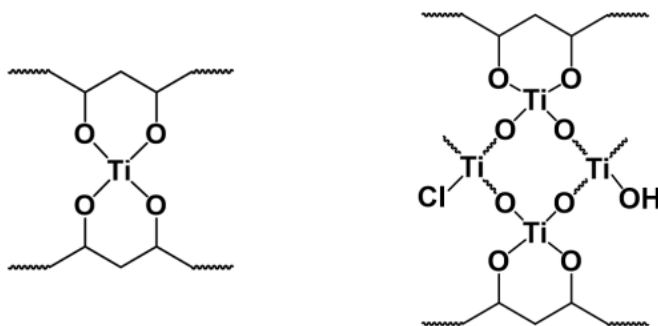


Figure 2.2.2 Proposed Structures of Titanium Oxide Hydrate/PVA hybrids. It is expected that a six membered ring is formed between titanium and PVA regardless of the titanium oxide hydrate species being mononuclear or polynuclear (11).

While no research has been done on the stability of titanium oxide hydrate/polyalcohol hybrids, the similar chemical structures of glycerol and PVA suggests that their interaction with titanium oxide hydrate would be similar. Comparing the stabilities of polyalcohols that form five-membered versus six-membered rings with titanium oxide hydrate may clarify which ring size is favored in polyalcohol hybrids.

2.3 Applications of Titanium Oxide Hydrate Hybrids

Most of the existing applications of titanium oxide hydrates are via the production of hybrid films. It has been shown that titanium oxide hydrate/PVA hybrid films have applications in optical devices, such as Distributed Bragg Reflectors for light or heat management (11,13). Application of other titanium oxide hydrate hybrids were only proposed and have not been extensively developed. For example, titanium/citric acid complexes may have biological uses, such as anticancer or antimicrobial agents (14). On the other hand, titanium oxide hydrate/polyalcohol hybrids might be used in UV light detectors or photocatalysts (4).

One application of titanium oxide hydrate/polyalcohol hybrids that has yet to be explored is as electrolytes for photo-rechargeable batteries. Examples of current photo-rechargeable batteries include dye-sensitized solar cells and bulk heterojunction solar cells, both requiring a separate energy storage device (2). A major limitation of these designs is inefficient connections between the energy

storage device and the solar cell. Photo-rechargeable redox flow batteries eliminate the need for such a connection because solar energy is stored by redox couples in liquid electrolytes that flow past electrodes (3). Advantages of this design include high lifetimes, low costs, and high energy storage (2).

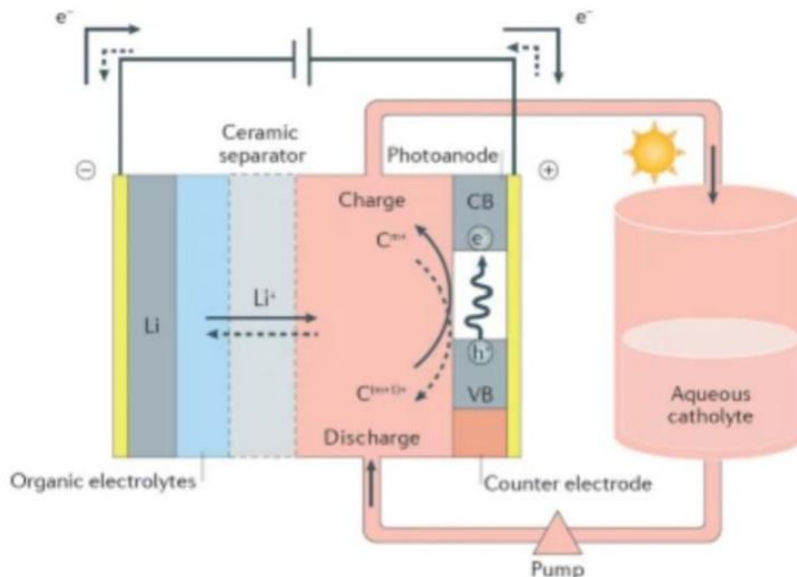


Figure 2.3.1 Photo-rechargeable Redox Flow Battery. Schematic of a photo-rechargeable redox flow battery utilizing lithium metal electrodes (3).

2.4 Redox Flow Batteries and Photo-rechargeable Redox Flow Batteries

The most common redox flow battery is the all-vanadium redox flow battery, first developed in 1988 (15). Despite their success and commercialization, all-vanadium redox flow batteries are expensive and have low energy density. They also rely on nonrenewable energy sources for charging, so there is an effort to develop cheaper, higher-power, and more sustainable alternatives. While there has been progress by utilizing polymer-based electrolytes for a low-cost yet highly

reversible redox flow battery, there still is the drawback of relying on a nonrenewable energy source for charging (16). Photo-rechargeable redox flow battery overcome this by utilizing a renewable energy source for charging. Currently, photo-rechargeable redox flow batteries have been made with electrolytes of an all-inorganic redox couple, such as I^-/I_3^- , or an all-organic redox couple, such as quinone derivatives (3). Additional research into the long-term energy storage capabilities of these fuels as well as scaled-up production levels is necessary for their commercialization.

Hybrid electrolytes would combine the desirable properties of inorganic and organic components, such as high redox activity and low cost, respectively; however, there is limited research on the applications of such electrolytes in photo-rechargeable redox flow batteries. Li *et al.* described how organic additives, such as d-sorbitol, to vanadium electrolytes improve current densities by increasing the number of vanadium ions able to participate in redox reactions. Within these electrolytes, the d-sorbitol forms a complex with vanadium ions, akin to titanium oxide hydrate/polyalcohol complexes, or adsorbs to the electrode and act as a source of hydroxyl groups for the redox reaction (17). While this work was performed outside the context of a photo-rechargeable redox flow batteries, it provides an example of using electrolytes with inorganic and organic components to improve the performance of an redox flow battery.

Considering the current literature on titanium oxide hydrate hybrids and their applications, further research into titanium oxide hydrate/polyalcohol hybrids is needed to better understand their interactions and explain their resulting stability,

photochromism, and electrochemical properties. There exists no work on the photoreduction of titanium in organic species and whether polyalcohol is involved in this electron transfer process. In addition, current photo-rechargeable redox flow batteries may benefit from the utilization of hybrid fuel. The research of this thesis will fill the knowledge gap concerning titanium oxide hydrate/polyalcohol hybrids and explore their applications as photochemically active electrolytes.

3. Materials and Methods

3.1 Titanium Oxide Hydrate/Polyalcohol Hybrid Preparation

Materials for titanium oxide hydrate/polyalcohols hybrid solutions were purchased from Sigma-Aldrich. Titanium oxide hydrates were synthesized by the procedure described by Russo *et al.* (6). Synthesis of titanium oxide hydrates for nuclear magnetic resonance (NMR) spectroscopy measurement modified this procedure by hydrolyzing TiCl_4 within deuterium oxide instead of deionized water. Reducing the water content within titanium oxide hydrates minimized undesirable water impurities within the NMR spectra.

For NMR spectroscopy and gas chromatography mass spectrometry (GC-MS), titanium oxide hydrate/polyalcohol hybrids were prepared with a 5:1 molar ratio of polyalcohol to titanium oxide hydrate. Hybrids for NMR spectroscopy contained the titanium oxide hydrates prepared with deuterium oxide while hybrids for GC-MS contained standard titanium oxide hydrates. This molar ratio of polyalcohol to titanium oxide hydrate was selected to avoid an overwhelming signal of uncoordinated polyalcohol. A slight excess of polyalcohol was included to increase the hybrid's stability and allow for multiple polyalcohol molecules to coordinate to the titanium oxide hydrate complex. For titanium oxide hydrate/glycerol hybrids, specific quantities were 1 mL of 1M titanium oxide hydrate solution and 0.46 g of glycerol. Hybrids were stored at 0°C until use to avoid TiO_2 precipitation.

Titanium oxide hydrate/polyalcohol hybrids for optical characterization and H-cell experiments were prepared in 20 mL volumes and consisted of 0.1M titanium oxide hydrate. 1.169 g of sodium chloride (NaCl) was dissolved in deionized water, so the final hybrid volume had a concentration of 1M NaCl. Next, the polyalcohol was added, and the mixture was stirred until homogeneous. The mass of polyalcohol was calculated so that the hybrid contained a 90:1 molar ratio of polyalcohol titanium oxide hydrate. Such a high ratio was used to maximize interactions between the polyalcohol and titanium complexes, improving the stability of the hybrid solution against TiO₂ precipitation. Lastly, 2 mL of 1M titanium oxide hydrate solution was added, and the hybrid was allowed to stir for at least 30 minutes. Exact quantities of deionized water and polyalcohol varied depending on the polyalcohol identity and desired concentration of titanium oxide hydrate. For example, a titanium oxide hydrate/glycerol hybrid consists of 4.3 g deionized water and 16.6 g glycerol.

Cyclic voltammetry utilized titanium oxide hydrate/polyalcohol hybrids with a concentration of 0.01M titanium oxide hydrate. A lower concentration of titanium oxide hydrate was chosen to minimize overpotentials from mass transfer limitations (19). For these hybrids, 200 μ L of 1 M titanium oxide hydrate solution was added to the hybrid, and in the case of the titanium oxide hydrate/glycerol hybrid, 17.9 g of deionized water and 1.6 g of glycerol were included as well. Titanium oxide hydrate/polyalcohol hybrids for optical characterization, H-cell experiments, and cyclic voltammetry were stored at room temperature in a drawer.

If the hybrid became cloudy, indicating that the titanium oxide hydrates had precipitated into TiO_2 , then it was discarded.

3.2 Organic Species Identification

Organic species in titanium oxide hydrate/glycerol hybrids before and after UV illumination were identified with NMR spectroscopy and GC-MS to propose a photoreduction mechanism for titanium oxide hydrate within these materials.

Titanium oxide hydrate/polyalcohol hybrids with 0, 10, 30, 60, and 120 minutes of UV illumination were characterized with ^1H NMR spectroscopy. UV illumination was performed with an Omnicure S1500 spot UV curing system at 100% power. The system utilized a 200W Mercury lamp and a 320-500nm wavelength filter. NMR measurements were performed on a 400MHz Bruker NMR spectrometer in Georgia Tech's NMR Center. Twenty-five mg of hybrid was dissolved in 0.7mL of deuterium oxide solvent and transferred to an NMR tube. The deuterium oxide solvent contained 0.9 wt% sodium trimethylsilyl propionate (TSP) NMR standard to reference spectra. Sixteen scans were performed for each measurement with the spectrometer at room temperature. NMR spectra were analyzed with MestreNova NMR software.

In addition to NMR spectroscopy, organic species in titanium oxide hydrate/glycerol hybrids were identified with GC-MS. This technique was chosen instead of standard mass spectrometry because it separates and then characterizes organic species, necessary because these hybrids contained a mixture of organic species. Titanium oxide hydrate/glycerol hybrids experienced 0

or 120 minutes of UV illumination with the Omnicure S1500 UV curing system and were sent to the Mass Spectrometry Core Center at Georgia Tech for analysis by their chemists with a ISQ 7610 GC-MS. Organic species were identified by referencing GC-MS data with NIST's Mass Spectral Data Center (18).

3.3 Optical Characterization

Ultraviolet-visible (UV-VIS) spectroscopy characterized the photochromic behavior of titanium oxide hydrate/polyalcohol hybrids prepared with various polyalcohols. Aliquots of titanium oxide hydrate/polyalcohol hybrids were exposed to 0, 1, 5, 10, or 60 minutes of UV illumination with the Omnicure S1500 UV curing system.

UV-VIS spectroscopy measurements were conducted with a Cary 5000 UV-Vis/NIR spectrophotometer. The instrument was first calibrated so that the baseline was the absorbance of DI water. Then, 1 mL of hybrid at an illumination time was added to a fresh plastic cuvette before its absorbance was measured with wavelengths from 200-800nm. Although a large wavelength range was measured, absorbance data was limited to 400-700nm, the visible light range, to describe the visible color change of these hybrids.

3.4 Electrochemical Characterization

Voltage generation of titanium oxide hydrate/polyalcohol hybrids during UV illumination was measured with an Agilent 34401A digital multimeter. A MATLAB

function, developed by undergraduate researchers Alex Chen and Brandon Perry within the Stingelin group at Georgia Tech, was utilized to take automated voltage measurements every 60 seconds. Voltage versus UV illumination time experiments used a glass H-cell in which half of the cell contained 9 mL of a 1M aqueous NaCl solution while the other half contained 9 mL of a fresh titanium oxide hydrate/polyalcohol hybrid. A single graphite rod electrode was inserted into each side of the H-cell and connected to the multimeter. The H cell was placed so that the hybrid side of the cell was 10 cm away from and centered with the UV lamp lead. UV illumination was applied to the hybrid for 60 minutes, during which its voltage was measured.

Equally interesting was titanium oxide hydrate/polyalcohol hybrids' ability to store their voltage after UV illumination. For these experiments, 9 mL of hybrid was placed in a sealed vial and illuminated with UV light for 60 minutes. Immediately after illumination, the hybrid was transferred to the hybrid side of the H-cell. Voltage measurements were taken for 12 hours following the method described above except no additional UV illumination was applied.

A CH Instruments CH1660D Electrochemical Workstation was used for cyclic voltammetry. BASI Graphite rod electrodes were used as working and counter electrodes while a BASI Ag/AgCl electrode served as the reference electrode. Between experiments, the graphite rod electrodes were cleaned by sonicating in IPA and DI water. The Ag/AgCl electrode was thoroughly rinsed with DI water after each use.

Titanium oxide hydrate/polyalcohol hybrid for cyclic voltammetry were sparged with argon gas for 15 minutes to reduce the dissolved oxygen concentration. If an illuminated hybrid was used, it was sparged for 15 minutes and transferred to a sealed vial before experiencing 60 minutes of UV illumination. All cyclic voltammetry measurements use a scan rate of 100 mV/s and 20 scan cycles were performed each measurement.

4. Results

4.1 Titanium Oxide Hydrate Photoreduction Mechanism

As introduced in chapter 2, the photoreduction of titanium oxide hydrate within titanium oxide hydrate/polyalcohol hybrids has remained unexplored in literature. Understanding this photoreduction mechanism is of interest to identify if the polyalcohol participates within redox reactions. A redox-active polyalcohol indicates a change in organic species after UV illumination, which can explain the unique electrochemical and optical properties of the illuminated hybrid compared to the hybrid before UV illumination.

NMR spectroscopy initially characterized organic species before and after UV illumination. Figure 4.1 illustrates the NMR spectra for titanium oxide hydrate/glycerol species with various UV illumination times.

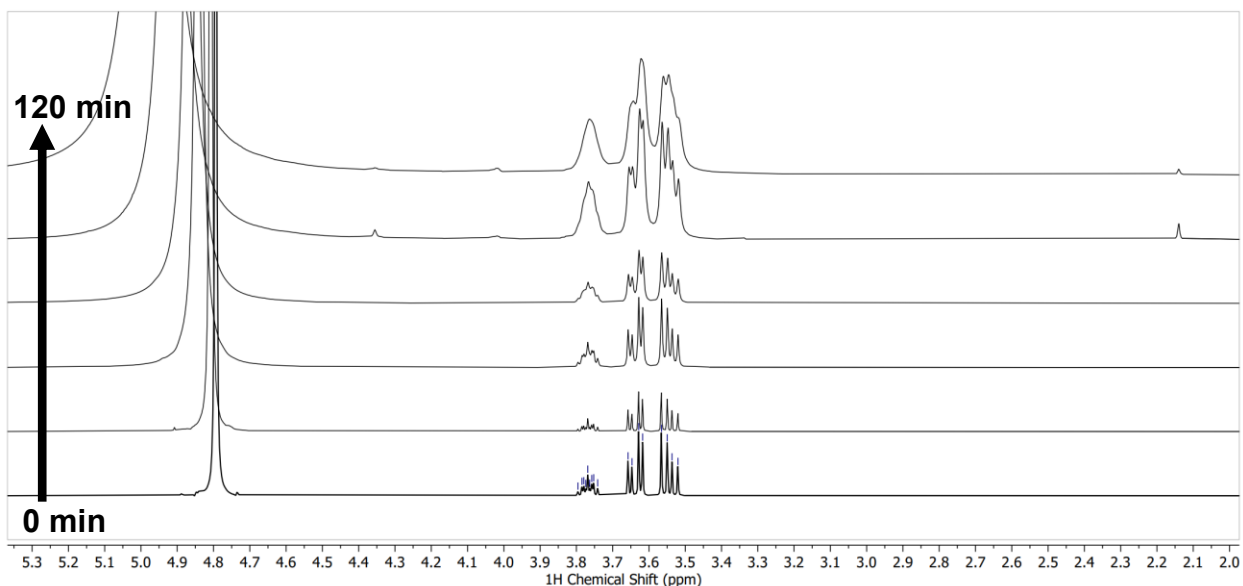


Figure 4.1 NMR Spectra of Titanium Oxide Hydrate/Glycerol Hybrids. Hybrids were illuminated with 0, 10, 30, 60, or 120 minutes of UV illumination.

From Figure 4.1, increasing UV illumination times causes broadening of peaks within the NMR spectra. This broadening is attributed to a greater presence of a paramagnetic species, titanium(III), instead of the diamagnetic titanium(IV). Paramagnetic species cause broadening of NMR signals due to relaxation times that are less than data acquisition times (20).

In addition, Figure 4.1 demonstrates the appearance of new peaks in the NMR spectra of titanium oxide hydrate/glycerol hybrids with UV illumination. Note that the unilluminated hybrid had no significant differences in peak positions as neat glycerol. Therefore, the presentation of results in this section will focus on the peaks that arise after UV illumination. New peaks indicate the appearance of new organic species within the hybrid due to UV illumination and suggest that the polyalcohol is redox active. These peaks appear at chemical shifts of 2.1 ppm, 4 ppm, and 4.1 ppm and are most visible in the hybrid with 120 minutes of UV illumination. The chemical shifts could belong to several different functional groups, such as alkyl or alcohol groups, and cannot be conclusively identified with only NMR spectroscopy.

Titanium oxide hydrate/polyalcohol hybrids prepared with polyalcohols other than glycerol have similar trends within their NMR spectra. Figure 4.2 contains the NMR spectra for hybrids prepared with ethylene glycol, 1,2-propanediol, or 1,3-propanediol and illuminated with UV light for 0 or 120 minutes.

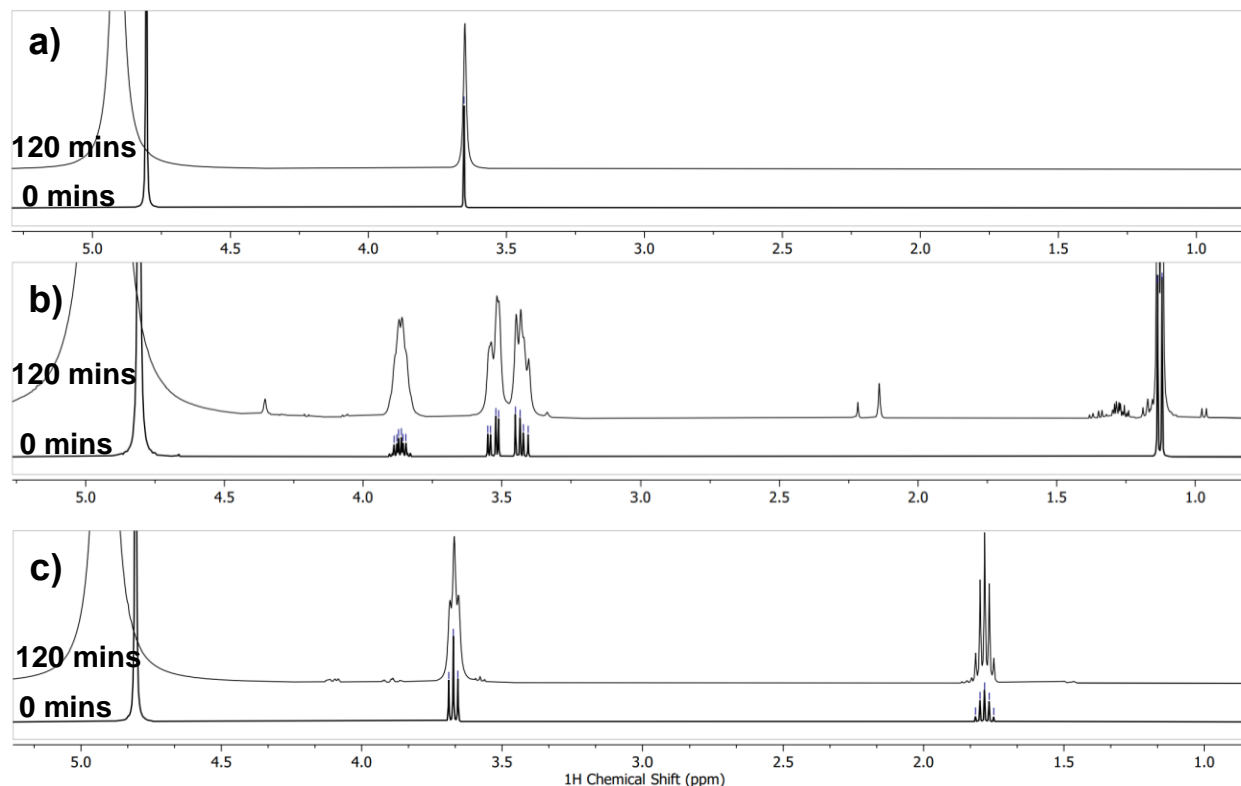


Figure 4.2 NMR Spectra of Titanium Oxide Hydrate/Polyalcohol Hybrids. Polyalcohols used in hybrid preparation were ethylene glycol (a), 1,2-propanediol (b), or 1,3-propanediol hybrids. The top spectrum for each polyalcohol is the hybrid with 120 minutes of UV illumination time while the bottom spectrum is the hybrid with no UV illumination.

Like titanium oxide hydrate/glycerol hybrids, UV illumination in the hybrids within Figure 4.2 resulted in peak broadening and the appearance of new peaks within the NMR spectra. Interestingly, the chemical shift and intensity of these new peaks depended on the polyalcohol's identity within the hybrid. Hybrids prepared with ethylene glycol and 1,3-propanediol had no or minimal appearance of peaks within the illuminated hybrid's NMR spectra. Conversely, new peaks in the illuminated titanium oxide hydrate/1,2-propanediol hybrid were greater in intensity than those in the ethylene glycol and 1,3-propanediol hybrids. Additionally, new

peaks in the titanium oxide hydrate/1,2-propanediol hybrid had similar chemical shifts as the new peaks in the titanium oxide hydrate/glycerol hybrid, suggesting similar functional groups. These findings suggest that the identity and stability of new organic species depends on the polyalcohol within the hybrid. Glycerol and 1,2-propanediol resulted in new organic species with similar functional groups and stability while ethylene glycol and 1,3-propanediol had new organic species with lower stability.

NMR spectroscopy provided information about functional groups of organic species. To identify the organic species responsible for these new functional groups, GC-MS was employed. Here, titanium oxide hydrate/glycerol hybrids were studied since they had the greatest intensity of new peaks in NMR spectroscopy, indicating a greater concentration of new organic species. Figure 4.3 shows the total ion chromatograms for titanium oxide hydrate/glycerol hybrids with 0 or 120 minutes of UV illumination.

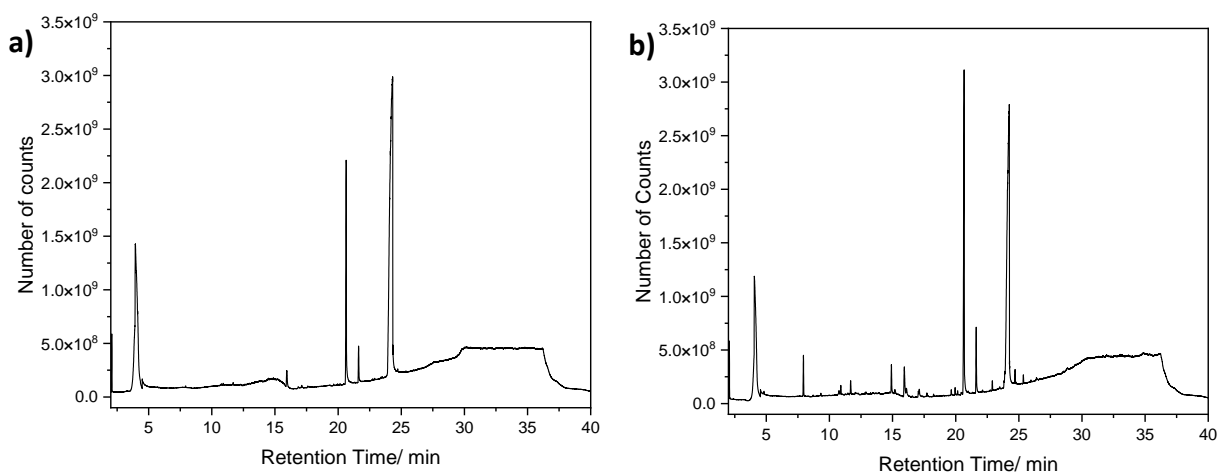


Figure 4.3 Total Ion Chromatograms of Titanium Oxide Hydrate/Glycerol Hybrids. Hybrids had 0 minutes (a) or 120 minutes (b) of UV illumination.

The total ion chromatograms in Figure 4.3 depict the number of species, each with a unique retention time, in the hybrids and their relative abundance. Importantly, the greater number of peaks in the illuminated hybrid's total ion chromatogram (Figure 4.3b) supports the previous claim that new species appear in Ti/glycerol hybrids after UV illumination. NIST's Mass Spectrometry Data Center was used to assign peaks in Figure 4.3 to organic species. Table 4.1 and 4.2 summarize the identified species and their structure for the titanium oxide hydrate/glycerol hybrid before and after UV illumination.

Table 4.1 Retention Time Assignments for Titanium Oxide Hydrate/Glycerol Hybrids without UV Illumination.

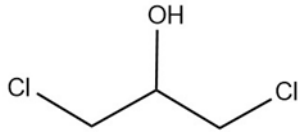
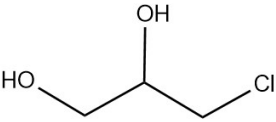
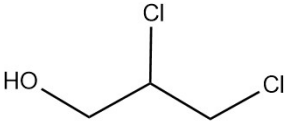
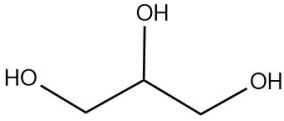
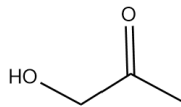
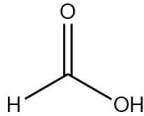
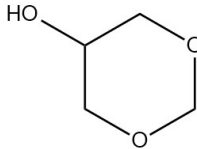
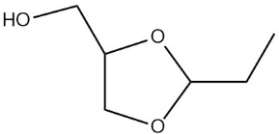
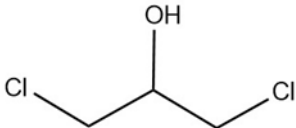
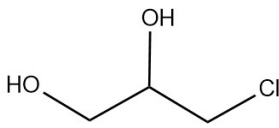
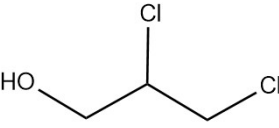
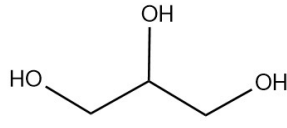
Retention Time (min)	Species Name	Structure
3.95	Hydrochloric acid	H-Cl
15.93	1,3-dichloropropan-2-ol	
20.64	3-chloropropane-1,2-diol	
21.62	2,3-dichloropropan-1-ol	
24.32	Glycerol	

Table 4.2 Retention Time Assignments for Titanium Oxide Hydrate/Glycerol Hybrids with 120 minutes of UV Illumination.

Retention Time (min)	Species Name	Structure
4.05	Hydrochloric acid	H-Cl
7.85	Hydroxyacetone	
11.69	Formic acid	
14.91	1,3-dioxan-5-ol	
15.21	2-ethyl-1,3-dioxolane-4-methanol	
15.93	1,3-dichloropropan-2-ol	
20.67	3-chloropropane-1,2-diol	
21.62	2,3-dichloropropan-1-ol	
24.24	Glycerol	

In Table 4.2, the peaks at 7.85 minutes and 11.69 minutes of retention time were assigned to hydroxyacetone and formic acid, respectively. Returning to NMR spectroscopy, these species can be assigned to peaks in the illuminated hybrid's NMR spectrum (Figure 4.1). Hydroxyacetone's methyl group is responsible for the peak at 2.1 ppm, and its methylene groups causes the singlet at 4.4 ppm. A singlet at 8.2 ppm also appears within this spectrum but is not pictured in Figure 4.1, which can be assigned to the aldehyde hydrogen of formic acid. Together, NMR spectroscopy and GC-MS confirm the presence of hydroxyacetone and formic acid in illuminated titanium oxide hydrate/glycerol hybrids.

Identifying hydroxyacetone and formic acid led to the proposed photoreduction mechanism in Figure 4.4. Hydroxyl radicals produced from the reduction of titanium(IV) to titanium(III) initially dehydrates glycerol into hydroxyacetone. Subsequent radical reactions could break down hydroxyacetone until it became formic acid.

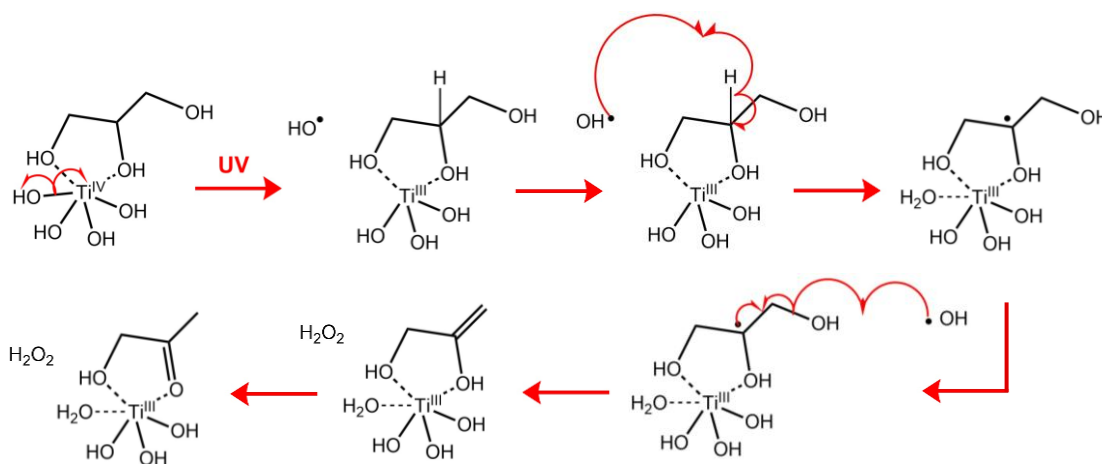


Figure 4.4 Proposed Photoreduction Mechanism of Titanium Oxide Hydrate within Titanium Oxide Hydrate/Glycerol Hybrids.

Moreover, GC-MS allowed for the identification of products from side reactions within illuminated titanium oxide hydrate/glycerol hybrids. Substitution reactions between chlorine anions and hydroxyl groups on glycerol resulted in molecules such as 3-chloropropane-1,2-diol with a retention time of 20.67 minutes in both hybrids. Acetalization between excess glycerol and formaldehyde in the illuminated hybrid led to cyclic structures like 1,3-dioxan-5-ol at 14.91 minutes of retention time. Furthermore, minor peaks with retention times beyond 17 minutes had no significant matches with NIST's mass spectroscopy database. The presence of side reactions and inability to assign all peaks emphasizes the complex chemistry and interaction of species within these material systems.

4.2 Electrochemical and Optical Properties

In addition to defining titanium's photoreduction mechanism, the optical and electrochemical properties of hybrids prepared with titanium oxide hydrate and glycerol, ethylene glycol, 1,2-propanediol, or 1,3-propanediol were explored. Hybrids prepared from various polyalcohols were characterized to determine the optimal polyalcohol to advance these hybrid systems as a photo-rechargeable redox flow battery electrolyte.

Most relevant for energy storage applications is the voltage generation and storage capabilities of titanium oxide hydrate/polyalcohol hybrids. Figure 4.5 illustrates the maximum voltage generated under UV illumination and the hybrid's ability to retain that voltage without constant illumination.

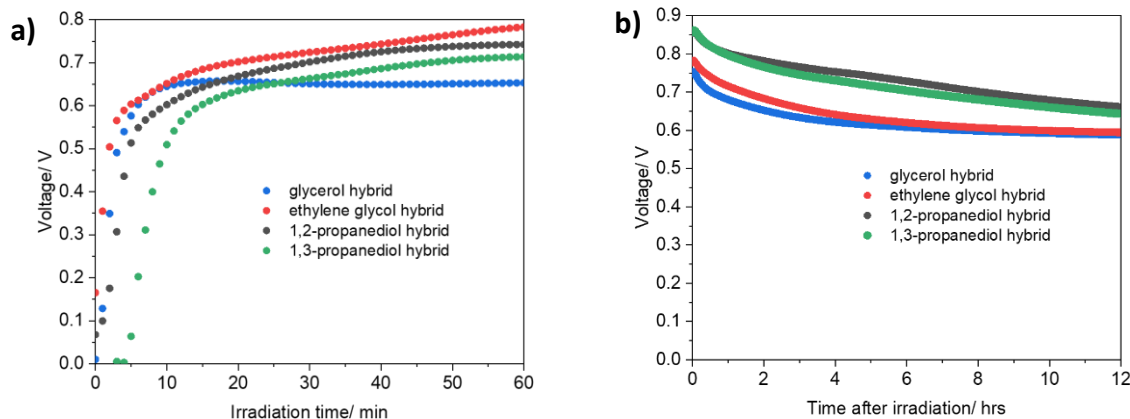


Figure 4.5 Titanium Oxide Hydrate/Polyalcohol Hybrid Voltage Generation and Storage. Voltage generated by titanium oxide hydrate/polyalcohol hybrids versus UV illumination time (a) and voltage storage of titanium oxide hydrate/polyalcohol hybrids versus time after UV illumination.

As shown in Figure 4.5a, the maximum voltage generated by a titanium oxide hydrate/polyalcohol hybrid depends on the polyalcohol identity. The titanium oxide hydrate/ethylene glycol hybrid had the highest voltage while the titanium oxide hydrate/glycerol hybrid had the lowest voltage. The low voltage produced by the titanium oxide hydrate/glycerol hybrid could be explained by the high viscosity of glycerol compared to ethylene glycol. Glycerol's high viscosity could create mass transfer limitations of the titanium oxide hydrate complexes to the electrode, resulting in a low voltage stored. Viscosity measurements on hybrids prepared with glycerol, ethylene glycol, 1,2-propanediol, or 1,3-propanediol to demonstrate significant viscosity differences between the hybrids and support this hypothesis.

Figure 4.5b demonstrates that titanium oxide hydrate/polyalcohol hybrids can not only generate voltage but effectively store that voltage for at least 12 hours. The voltage storage capability of these hybrids depended on the polyalcohol

identity. The voltage fade in hybrids with 1,2-propanediol or 1,3-propanediol showed a linear decrease while hybrids with glycerol and ethylene glycol had an asymptotic decline. Therefore, hybrids prepared with glycerol and ethylene glycol hybrids were more effective at retaining their voltage post UV illumination than hybrids with 1,2-propanediol or 1,3-propanediol.

The improved voltage storage capabilities of titanium oxide hydrate and glycerol or ethylene glycol hybrids suggests that the new organic species within these hybrids led to more stable titanium(III) complexes. To better understand the stability of these complexes in illuminated hybrids, optical properties of titanium oxide hydrate/polyalcohol hybrids were characterized. Although photochromic properties of titanium oxide hydrate/glycerol complexes have been characterized, comparing their photochromic response to other hybrids would provide insight into how the polyalcohol identity influences the stability of titanium(III) complexes. Figure 6 contains UV-VIS spectroscopy data for titanium oxide hydrate/polyalcohol hybrids with 60 minutes of UV illumination.

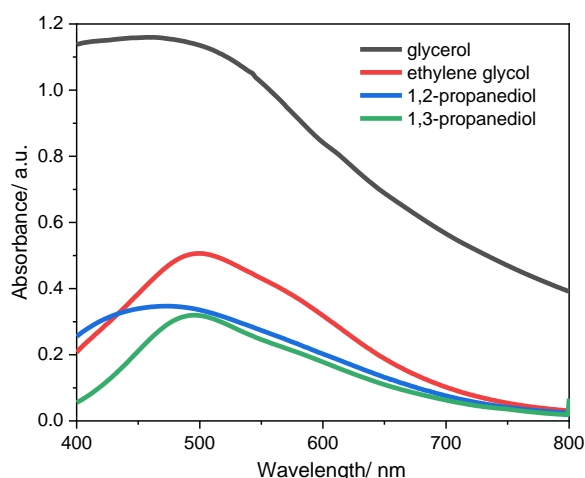


Figure 4.6 Absorbance of Illuminated Titanium Oxide Hydrate/Polyalcohol Hybrids.

Since titanium(III) follows Beer-Lambert's Law, its concentration is proportion to the hybrid's absorbance. The titanium oxide hydrate/glycerol hybrid having the highest maximum absorbance suggests that it would have the highest titanium(III) concentration and could stabilize titanium in its reduced state the best. As the absorbance decreases, then so could the hybrid's ability to stabilize titanium(III), with the titanium oxide hydrate/1,3-propanediol hybrid potentially providing the least stabilization.

Cyclic voltammetry measurements demonstrates the same stability trend. Figure 4.7 shows the onset potential of the oxidation peak of titanium(III) into titanium(IV) for titanium oxide hydrate/polyalcohol hybrids.

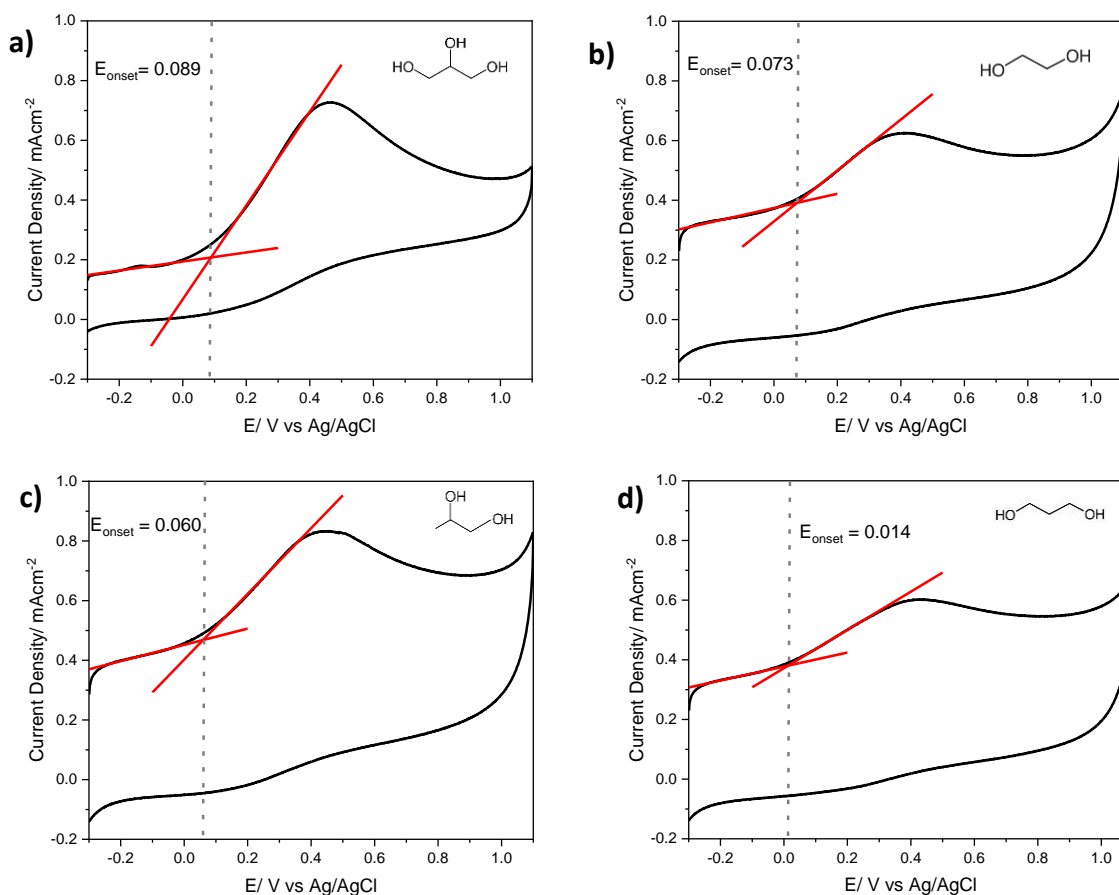


Figure 4.7 Cyclic Voltammograms of Titanium Oxide Hydrate/Polyalcohol Hybrids. Hybrids contains glycerol (a), ethylene glycol (b), 1,2-propanediol (c), or 1,3-propanediol (d) and were illuminated with UV light for 60 minutes. Measured currents were normalized by the surface area of the working electrode.

For each cyclic voltammogram in Figure 4.7, the onset potential of titanium(III) oxidation was found from the intersection of tangent lines of the baseline current and rising current of the oxidation peak. The titanium oxide hydrate/glycerol hybrid having the highest onset potential means that it would require the most energy to oxidize titanium(III), suggesting a more stable titanium(III) species. This onset potential decreases in the hybrids prepared with

other polyalcohols, with the titanium oxide hydrate/1,3-propanediol hybrid once again having the lowest onset potential and likely the lowest stability.

4. Discussion and Conclusions

The work within this thesis investigated titanium oxide hydrate/polyalcohol hybrids for photo-rechargeable battery electrolytes. A photoreduction mechanism for titanium oxide hydrate within titanium oxide hydrate/glycerol hybrids was proposed based on NMR spectroscopy and GC-MS findings. The application of titanium oxide hydrate/polyalcohol hybrids as photo-rechargeable battery electrolytes was then investigated through electrochemical and optical characterization. Together, these findings build on our understanding of titanium oxide hydrate/polyalcohol hybrids as photo-rechargeable battery electrolytes and have important implications for the material system moving forward.

Defining titanium oxide hydrate's photoreduction mechanism demonstrates that the polyalcohol is consumed by these reactions. It would be advantageous for polyalcohol fuels to initially contain a large excess of polyalcohol since its concentration is expected to decrease over time. The stability of the hybrid against TiO_2 precipitation and undesirable titanium(III) oxidation would also decrease as the polyalcohol is broken down in smaller organic molecules that may not chelate to the titanium oxide hydrate complex. Chelation to the titanium complex significantly improves the stability of titanium oxide hydrate as shown in studies with titanium oxide hydrate and citric acid complexes (8).

Consequently, the lifetime of the hybrid electrolyte will be dictated by the initial concentration of the polyalcohol unless fresh polyalcohol is added to the hybrid from a separate reservoir. For titanium oxide hydrate/glycerol hybrids, the high viscosity of glycerol would limit the practicality of this design since neat

glycerol would be difficult to pump. Glycerol could be diluted in water to improve its transport properties. However, the excess water would decrease the hybrid's titanium oxide hydrate to polyalcohol molar ratio, reducing the stability of titanium complexes and electrolyte lifetime.

Characterization of the optical and electrochemical properties of titanium oxide hydrate/polyalcohol hybrids illustrate the nuance when choosing a polyalcohol for a hybrid electrolyte. Titanium oxide hydrate/glycerol hybrids had the highest stability of titanium(III) complexes from UV-VIS spectroscopy and cyclic voltammetry data, suggesting improved long-term energy storage. The low voltage produced by titanium oxide hydrate/glycerol hybrids indicates that a photo-rechargeable redox flow battery with this electrolyte would have a low energy density and require more battery cells to store the same amount of energy as high energy density battery technologies. Titanium oxide hydrate/ethylene glycol hybrids overcome this challenge by storing larger voltages. While voltage storage experiments demonstrate a similar decrease for hybrids with glycerol and ethylene glycol, cyclic voltammetry and UV-VIS spectroscopy show a greater stability of titanium(III) within titanium oxide hydrate/glycerol hybrids. Therefore, there is no optimal polyalcohol for titanium oxide hydrate/polyalcohol hybrid electrolytes as each polyalcohol has its advantages and disadvantages.

Before these material systems can be used as widespread photo-rechargeable redox flow battery electrolytes, additional study is necessary. First, photoreduction mechanisms for titanium oxide hydrate within hybrids of ethylene glycol, 1,2-propanediol, or 1,3-propanediol should be developed. Identifying the

organic species resulting from these mechanisms would add to the discussion on the stability of titanium(III) within these hybrids.

Hybrid viscosity experiments would also explain titanium(III) stability. Viscosities of neat polyalcohols as well as hybrids should be characterized to solidify if the polyalcohol identity has a significant impact on the hybrid viscosity. High viscosity could be beneficial for hybrid voltage storage since it would limit the mass transfer of oxygen gas, which drives the oxidation of titanium(III). On the other hand, high viscosities could be detrimental to the maximum voltage generated upon UV illumination, as seen for titanium oxide hydrate/glycerol hybrids.

Finally, cycling measurements should be performed on titanium oxide hydrate/polyalcohol hybrids to determine their reversibility as well as stability against TiO_2 precipitation with continuous use. Cycling experiments would pair nicely with complete photoreductions mechanisms for each titanium oxide hydrate/polyalcohol hybrid. Photoreduction mechanisms with organic products that can chelate to titanium oxide hydrate are expected to result in more stable titanium oxide hydrate complexes and photo-rechargeable redox flow battery electrolytes that can be cycled for longer periods of time.

The knowledge gained from this thesis supports the development of titanium oxide hydrate/polyalcohol hybrids into photo-rechargeable battery electrolytes. Future experiments will build on this foundation to develop a practical photo-rechargeable battery electrolyte. Critically, the widespread adoption of this

emerging energy storage technology will encourage the use of solar energy to sustainably meet growing global energy consumption.

5. References

1. *Executive summary – Electricity Mid-Year Update: July 2024 – Analysis*. IEA. <https://www.iea.org/reports/electricity-mid-year-update-july-2024/executive-summary>.
2. Schmidt, D.; Hager, M. D.; Schubert, U. S. Photo-Rechargeable Electric Energy Storage Systems. *Advanced Energy Materials* **2015**, 6 (1), 1500369. <https://doi.org/10.1002/aenm.201500369>.
3. Park, M.; Ryu, J.; Cho, J. Material Design and engineering of next-generation flow-battery technologies. *Nat Rev Mat.* **2017**, 2. DOI:10.1038/natrevmats.2016.80.
4. Russo, M. Titanium Oxide Hydrates: Optical Properties and Applications. Ph.D. Thesis. University of London, London, England, **2009**.
<https://qmro.qmul.ac.uk/xmlui/handle/123456789/597>.
5. Baura-Pena M.P.; Martinez-Lope M.J.; Garcia-Clavel M.E. Synthesis and characterization of a hydrated titanium(IV) oxide. *Thermochimica Acta.* **1990**, 179, 89-97. DOI: 10.1016/0040-6031(91)80337-I.
6. Russo, M.; Rigby, S. E. J.; Caseri, W.; Stingelin, N. Pronounced Photochromism of Titanium Oxide Hydrates (Hydrous TiO₂). *J. Mater. Chem.* **2010**, 20 (7), 1348–1356. DOI: 10.1039/B917152E.

7. Russo, M.; Rigby, S.; Caseri, W.; Stingelin, N. Versatile Chromism of Titanium Oxide Hydrate/Poly(vinyl alcohol) Hybrid Systems. *Adv. Mat.* **2012**, 24, 3015-3019. DOI: 10.1002/adma.201200603.
8. Kakihana, M.; Kobayashi, M.; Tomita, K.; Petrykin, V. Application of Water-Soluble Titanium Complexes as Precursors for Synthesis of Titanium-Containing Oxides via Aqueous Solution Processes. *Bull. Chem. Soc. Jpn.* **2010**, 83, 1285-1308. DOI: 10.1246/bcsj.20100103.
9. Livage, J.; Henry, M.; Sanchez, C. Sol-gel chemistry of transition metal oxides. *Prog. Solid St. Chem.* **1968**, 18, 259-341. DOI: 10.1016/0079-6786(88)90005-2.
10. Torgunrud, J.; Faria, A.; Miller, S. Thermodynamics of silica depolymerization with alcohols. *Polyhedron.* **2020**, 187. DOI: 10.1016/j.poly.2020.114562.
11. Balzer, A. Structure-Property Interrelations of Polymers for Photonics and Electronics. Ph.D. Thesis. Georgia Institute of Technology, Atlanta, GA. **2022**. <http://hdl.handle.net/1853/66620>.
12. Russo, M.; Rigby, S.; Caseri, W.; Stingelin, N. Versatile Chromism of Titanium Oxide Hydrate/Poly(vinyl alcohol) Hybrid Systems. *Adv. Mat.* **2012**, 24, 3015-3019. DOI: 10.1002/adma.201200603.
13. Bachevillier, S.; Yuan, H.; Strang, A.; Levitsky, A.; Frey, G. L.; Hafner, A.; Bradley, D. D. C.; Stavrinou, P. N.; Stingelin, N. Fully Solution-Processed Photonic Structures from Inorganic/Organic Molecular

- Hybrid Materials and Commodity Polymers. *Adv. Fun.I Mat.* **2019**, 29 (21), 1808152. DOI:10.1002/adfm.201808152.
14. Paradies, J.; Crudass, J.; MacKay, F.; Yellowlees, L. J.; Montgomery, J.; Parsons, S.; Oswald, I.; Robertson, N.; Sadler, P. J. Photogeneration of Titanium(III) from Titanium(IV) Citrate in Aqueous Solution. *Journal of Inorganic Biochemistry* **2006**, 100 (7), 1260–1264. DOI: 10.1016/j.jinorgbio.2006.02.011
15. Rychcik, M.; Skyllas-Kazacos, M. Characteristics of a New All-Vanadium Redox Flow Battery. *Journal of Power Sources* **1988**, 22 (1), 59–67. DOI: 10.1016/0378-7753(88)80005-3.
16. Janoschka, T.; Martin, N.; Martin, U.; Friebe, C.; Morgenstern, S.; Hiller, H.; Hager, M. D.; Schubert, U. S. An Aqueous, Polymer-Based Redox-Flow Battery Using Non-Corrosive, Safe and Low-Cost Materials. *Nature* **2015**, 527 (7576), 78–81. DOI: 10.1038/nature15746.
17. Li, S.; Huang, K.; Liu, S.; Fang, D.; Wu, X.; Lu, D.; Wu, T. Effect of Organic Additives on Positive Electrolyte for Vanadium Redox Battery. *Electrochimica Acta* **2011**, 56 (16), 5483–5487.
18. *Mass Spectrometry Data Center, NIST*. chemdata.nist.gov. <https://chemdata.nist.gov/>.
19. Neyhouse, B. J.; Brushett, F. R. From the Synthesis Vial to the Full Cell: Electrochemical Methods for Characterizing Active Materials for

Redox Flow Batteries. *Encyclopedia of Energy Storage* **2022**, 453–465. DOI:10.1016/b978-0-12-819723-3.00058-5.

20. Lehr, M.; Paschelke, T.; Trumpf, E.; Vogt, A.; Näther, C.; Sönnichsen, F. D.; McConnell, A. J. A Paramagnetic NMR Spectroscopy Toolbox for the Characterisation of Paramagnetic/Spin-Crossover Coordination Complexes and Metal–Organic Cages. *Angewandte Chemie International Edition* **2020**, 59 (43), 19344–19351.
DOI:10.1002/anie.202008439.