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Electronic effects of substituents on redox shuttles for overcharge protection of li-ion batteries

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ELECTRONIC EFFECTS OF SUBSTITUENTS ON REDOX SHUTTLES FOR OVERCHARGE PROTECTION OF LI-ION BATTERIES

A thesis presented

by

Mehmet NurullahAtes

to

The Department of Chemistry and Chemical Biology

In partial fulfillment of the requirements for the degree of

Master of Science

in the field of

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ABSTRACT OF THESIS

Submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry in the Graduate School of Northeastern University, April, 2012

The redox behavior and kinetic parameters of five ferrocene derivatives were investigated in an electrolyte comprised of 1M LiPF₆ in 50:50 volume percent EC:EMC (ethylene carbonate: ethyl methyl carbonate), a typical electrolyte used in lithium-ion batteries. Using cyclic voltammetry (CV) and rotating disc electrode voltammetry (RDE) techniques, the effect of electron donating and withdrawing substituents on each derivative was evaluated from the view point of the Hammett substituent constant. The reaction rate constants and exchange current densities were determined as a function of the Hammett constants. A useful comparison between two Hammett approaches, which was based on CV and RDE results, were established versus oxidation potential for each derivative. We found that electrochemical rate constants of the ferrocene derivatives can be related to the Hammett equation which gives an accurate approximation for predicting the oxidation potential of redox shuttles when changes are desired in their electron donating and electron withdrawing properties by means of functional group substitution. Our results show that the exchange current density and reaction rate for oxidation decrease as the electron withdrawing property of the substituent increases. It is also shown that electron donating and electron withdrawing properties of a substituent affect the exchange current density and electrochemical oxidation reaction rate obeying a trend opposite to that of the Hammett substituent constants (σ). The correlations found here are expected to improve the ability to systematically design chemical overcharge protection reagents through judicious substitution of functional groups on redox shuttles.

The first chapter provides an introduction to lithium ion (Li-ion) battery basics and its importance as an alternative renewable energy source to meet the global energy demand. After a brief, general, perspective on lithium battery principles, the first Chapter continues with a discussion of safety issues of Li-ion batteries. Finally, it ends with a discussion of the fundamental mechanism of overcharge protection of Li-ion batteries, along with theoretical aspects of chemical redox shuttles which are developed to overcome the overcharge-related safety concerns of these batteries.

Presented in the second chapter are experimental procedures employed in this work, followed by a detailed discussion of the results obtained from cyclic voltammetry and rotating disc electrode studies of redox shuttle reagents.

The final, third chapter, concludes with ramifications of this research and mentions a brief discussion of future research directions.

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and no time was too busy for him to respond to my questions. His guidance and deep knowledge kept me busy and inspired me to become like him. Late night experiments are the most enjoyable moments that I missed after his marriage to Ashley.

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List of Abbreviations and Symbols

α	Charge Transfer Coefficient
η	Overpotential
ω	Angular Frequency
σ	Hammett Substituent Constant
ρ	Reaction Constant for Hammett Equation
υ	Kinematic Viscosity of the Electrolyte
η	Dynamic Viscosity
A	Electrode Area
С	Concentration
D	Diffusion Coefficient
D _E	Potential Differences
e-	Electron
E _p	Peak Potential
$E_{p/2}$	Half Peak Potential
F	Faraday's Constant
io	Exchange Current Density
I_{pa}	Anodic peak
I _{lim}	Limiting Current
k	Heterogeneous Rate Constant
К	Equilibrium Constant
n	Number of electrons
Т	Temperature

Scan Rate

CV	Cyclic Voltammetry
GC	Glassy Carbon
OCV	Open Circuit Voltage
RDE	Rotating Disk Electrode
RE	Reference Electrode
WE	Working Electrode
EV	Electrical Vehicles
HEV	Hybrid Electrical Vehicles
PHEV	Plug-in Hybrid Electrical Vehicles
LIB	Lithium-Ion Battery
PTC	Positive Thermal Coefficient
EC	Ethylene Carbonate
EMC	Ethyl Methyl Carbonate

v

Chapter 1

Introduction

1. Introduction

1.1.Global Energy Demand

The most serious challenge facing an ever growing world population, expected to reach about 10 billion by 2050 from today's 7 billion, is new sources of energy, and ways of storing the energy. Renewable energy sources such as wind and solar power require efficient and low cost means of storing them for use during periods when they are not abundant or unavailable. In this respect, batteries are expected to play a major role. Batteries are also indispensable for our everyday life. The modern interconnected world made possible via sleek smart phones, personal tablets, laptop computers, and internet on-the-go would not have been possible without the successes achieved in the past thirty five years in the research and development of rechargeable lithium batteries. Li-ion batteries, the latest incarnation of these devices, in various sizes and shapes, have become household items which are nothing of short of spectacular when it is considered that they were mere laboratory curiosities a couple of decade ago. Lithium ion batteries are characterized by high voltages and capacities which translate into energy densities significantly higher than that of conventional lead-acid, nickel-metal hydride and nickel-cadmium batteries. According to a market research study of lithium batteries, more than a billion Li-ion battery cells have been manufactured for cellular phones, laptop computers and other portable devices encompassing a world market of about 10 billion US dollars.⁽²⁾⁽³⁾⁽⁴⁾⁽⁵⁾⁽⁶⁾

The Ragone Chart in figure 1 provides energy versus power comparison of established and emerging battery technologies. Lithium ion batteries offer more than three times the energy densities than conventional aqueous power sources, and the increasing energy density trend for rechargeable lithium batteries is expected to continue in the foreseeable future. The future interest in Li-ion batteries is expected to grow exponentially as they become increasingly used for transportation applications including hybrid electric vehicles (HEV), plug-ion hybrid electric vehicles (PHEV) and all-electric vehicles (EV). According to a recent report, more than fifty percent of vehicles will be comprised of EVs, PHEVs or HEVs by the year 2030.



Figure 1.1Ragone plot demonstrates energy density vs. power density for various battery energy sources.⁽⁷⁾

Currently, more than 90 percent of HEVs are run with Ni-MH batteries, however in the next 20 years, the predominant part of the PHEVs, HEVs and EVs vehicles are anticipated to use Lithium ion batteries. This is the major motivation behind developed countries currently investing on rechargeable battery research. The Li-ion battery market size is expected to reach about \$50 billion by 2030.⁽⁴⁾⁽⁸⁾

1.2. Lithium-Ion Batteries

A battery converts electrochemical energy stored in the active materials in its negative and positive electrodes into electrical energy. This process involves electron transfer from one active material to the other via an external electric circuit while ions are transported across the electrodes within the battery through the electrolyte. A battery has three parts⁽⁹⁾:

a) Cathode or positive electrode which is electrochemically reduced during the discharge reaction.

b) Anode or negative electrode in which the active material is oxidized to generate electrons and ions during discharge.

c) Electrolyte, which, depending on the battery type is solid or liquid, conducts the ions generated at the anode towards the cathode to combine with it and the electrons are transported though the external load to complete the electrochemical reaction during battery discharge.

Batteries can be classified into two major types depending on whether they are nonrechargeable (primary) or rechargeable (secondary). A schematic diagram for a rechargeable lithium ion battery cell is shown Figure 1.2.



Figure 1.2. Schematic diagram of lithium ion batteries.⁽³⁾

Lithium ion batteries (LIBs) have several advantageous over other rechargeable batteries such as NiMH or NiCd batteries⁽⁹⁾;

a) They possess higher cell voltage (up to 4V)

b) Higher energy density resulting from the high cell voltage and capacity (up to about

200 Wh/kg /h or 500Wh/Liter)

c) They have no memory effect

d) They exhibit longer lifespan (5-10 years)

Despite these various advantages, Li-ion batteries have a propensity for safety hazards which originate from their chemistry and high energy density. In 1995, an Apple PowerBook 5300 got overcharged and caught fire while it was being tested for inadvertent abuse conditions. After that

Apple withdrew lithium batteries from its computers until several years later when they became convinced that the safety of Li-ion batteries was significantly improved. In 2000, Dell recalled 27,000 LIBs which were used in their laptops, and subsequently other laptop manufacturers recalled LIBs from their computers as well.⁽¹⁰⁾As a result of these market losses; LIBs are now expected to pass a number of abuse tests before they are accepted for use in laptops and other portable electronic devices. These tests include; I) overcharging the battery beyond its voltage range II) external short circuiting III) mechanical tests such as crushing, dropping onto a concrete floor, and IV) heating in a hot box to an industry established high temperature.

1.3.Safety Issues

Perhaps the notion of lithium metal can bring some concerns to our mind. In fact, the early development of rechargeable Li metal anode based batteries did not lead to successful commercial products because of safety issues associated with them. In 1991, Sony replaced Li with a graphitic anode to overcome safety concerns of Li anode batteries, and the modern era of Li-ion batteries emerged to create the revolution in portable electronics. It should be noted that lithiated carbon and metallic lithium have very close redox potentials in lithium batteries which together with the light weight of carbon provides high energy densities for Li-ion batteries. A typical commercial Li-ion battery consists of graphite (C_6) anode and a lithiated metal oxide cathode, for example LiCoO₂, to provide a cell with a specific energy of about 200 Wh/kg and an energy density of 500 Wh/L. Another advantage of using graphite as anode is that the lithiated graphite (LiC₆) has much higher melting point than that of lithium metal which melts at 180 $^{\circ}C$.⁽¹⁰⁾ This translates into better safety characteristics for Li-ion batteries than those based on Li metal anodes. Nevertheless, the very high energy densities of Li-ion batteries make them

potentially unsafe, especially when abused. These conditions include short circuit, overcharge, over discharge, and mechanical impact.

1.3.1. Overcharge Protection

Overcharge protection of Li-ion batteries is necessary to prevent electrolyte degradation and to equalize the capacities of individual cells in a series connected battery pack ^(12, 13). The organic electrolyte used in a Li-ion battery, usually a solution of LiPF₆ dissolved in an organic carbonate solvent mixture (for example ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC)) is irreversibly oxidized if the battery cell is charged to a potential higher than its stability window. The oxidation of the electrolyte will degrade the performance of the battery, and, even more seriously, can cause safety hazards due to gas generation, excessive pressure buildup, and ensuing thermal runway reactions in the cell. In commercial battery packs, electronic circuitry keeps the end of charge voltage in the safe region. However, a chemical solution to this problem that can overcome the complexity of the electronics and its additional cost to the consumer is the use of redox shuttle reagents. They are materials dissolved in the electrolytes with reversible redox potentials slightly above that of the cathode, and they help lock the charge voltage of the cell at the oxidation potential of the chemical shuttle reagent if the cell experiences overcharge. In addition to protecting individual cells from overcharge, it is necessary to equalize the capacities of individual cells in a battery pack built from many cells connected in series to attain the high voltage necessary for applications such as powering laptop computers. In figure 1.3a general diagram demonstrating how a weak cell in a series-connected battery pack affects its safety is displayed.



Figure 1.3.Schematic illustration of overcharge mechanism. a) Fully discharged state of battery pack and b) not fully charged state while one of the weak cells is being fully charged. ⁽¹¹⁾. The weak cell prevents the normal cell from being fully charged. This must be overcome through cell capacity equalization in the charging process via electronics or redox shuttles.

There are three major methods to prevent a battery from overcharge abuse conditions: external voltage regulation by means of electronic circuitry, use of inactivation agents, and addition of redox reagents to the electrolyte. In an external electronic protection system, if the normal battery cell experiences overcharge, the external circuit will shunt the current generated during overcharge of the normal cell while the weak cell is being fully charged thereby bypassing the excessive charge that is a burden on lithium ion cells. In addition, external systems have the ability to prevent high temperature buildup by allowing the current to go through outside of the battery pack rather than inside the lithium ion cells. A main advantage of using this system in commercial applications is controlling the heat management. However, additional weight, volume and cost to the battery pack are predominant disadvantages of using external electronic circuitries. Another option for overcharge protection is using inactivating agents which can be advantageous because of the small amounts needed in the battery. One problem encountered in an external protection system is additional battery pack weight. However, these inactivating agents have not been demonstrated to work well in Li-ion batteries. The molecule used for this such as furan, biphenyl, and 3-chlorothiophene are very vulnerable to polymerization during normal charge , and thus their successful applications are questionable since after polymerization the material can easily create a barrier for lithium ion transport between cathode and anode active materials, which is undesirable. The comparison of these two protection methods can be seen in figure 1.4.

Characteristic	External voltage regulation	Inactivation agent
Mechanism	Electronic regulation. Reversible	Permanent inactivation of the overcharged cells by gassing and coating of insulator coating. Irreversible.
Physical device	Electric circuit	Electrolyte additive
Weight, volume, and cost	Disadvantage	Advantage
Heat generation	Electric work	Heat from chemical reactions of the additive
Thermal management	Advantage	Disadvantage

Figure 1.4. Comparison of two systems other than Redox Shuttles.⁽¹¹⁾

The third method of protecting the cell from overcharge and safety hazards is the use of chemical redox shuttle reagents already mentioned above. They are the subjects of this thesis.

1.4. Aim of Thesis

Bis-cyclopentadienyl iron (II) or more commonly known as ferrocene (Fc) is a standard redox reagent⁽¹⁴⁾ recommended by the International Union of Pure and Applied Chemistry (IUPAC)⁽¹⁵⁾ for calibration of Nernstian systems in organic solvent-based reaction media. In non-aqueous electrolytes, the ferrocene/ferrocenium (Fc/Fc⁺) couple, seen in Scheme 1, is Nernstian, soluble in many organic solvents, and possesses good thermal stability.^(16, 17)



Scheme 1: Ferrocene/Ferrocenium couple.

Given these advantages, ferrocene can be used as a redox reagent in non-aqueous media for overcharge protection of some lithium batteries as originally shown by Abraham et al⁽¹²⁾ and later by Golovin et al.⁽¹⁸⁾ In its role as a redox shuttle in a Li or Li-ion cell, ferrocene is oxidized at the positive electrode and the resulting ferrocenium product shuttles back to the negative electrode to be reduced and converted to its initial state.⁽¹²⁾ This reversible process, shown in Scheme 2, is called the oxidation-diffusion-reduction-diffusion cycle⁽¹¹⁾, abbreviated the O-D-R-D cycle. More cycles from the redox shuttle give better protection for the Li-ion battery.



Scheme 2. Ferrocene redox shuttle mechanism (O-D-R-D cycle).

In this thesis, we take advantage of the Nernstian redox behavior of a series of ferrocene/ferrocenium couples for a fundamental study of the role of electron withdrawing and donating substituents on the extent of potential shifts of chemical shuttle reagents and the kinetics of the underlying electrochemical reactions. A particular aim was to determine the relationship between the heterogeneous electron transfer rate constants relevant to electrochemical processes and the Hammett substituent constant, σ , described by Hammett,^(19, 20) which provides a quantitative measure of the contribution of a given substituent to the reaction kinetics. In this paper, we present electrochemical data obtained using rotating disc electrode

voltammetry (RDE) for a series of ferrocene derivatives and the determination of the relevant kinetic information from detailed analysis of this data. Some of the electrochemical information needed for this study was also obtained from cyclic voltammetry (CV) of the same ferrocene solutions. From the CV and RDE results, the relationship between the Hammett substituent constant (σ) and the oxidation peak potentials in heterogeneous (electrochemical) reactions has been established. The dependence of the heterogeneous reaction rate constant on the electron withdrawing and donating properties of the substituent on ferrocene has revealed that our results can provide a useful approach to the systematic design of overcharge protection reagents for rechargeable Li batteries.

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Chapter 2

Electronic Effects of Substituents on Redox Shuttles for Overcharge Protection of Li-Ion Batteries

2.1. Introduction

Overcharge protection of Li-ion cells is necessary whether they are used individually as in most cell phones, or as high energy battery packs in which two or more cells are connected in series and parallel to produce the required voltage and capacity. Its main purposes are: i) to prevent electrolyte degradation, ii) to equalize the capacities of individual cells in a seriesconnected battery pack to achieve long cycle life for the pack assembled from cells with small capacity differences, and iii)to prevent safety hazards originating from thermal runway reactions caused by electrolyte and electrode decomposition when the cells exceed a certain voltage limit during charge.⁽¹⁾Since organic electrolytes used in Li-ion batteries will oxidize at potentials above their electrochemical stability windows, it is important to maintain individual cell voltage below these potentials in order to achieve optimum battery performance and safety. To achieve long cycle life in a series-connected Li-ion battery pack, the capacities of individual cells have to be equalized during charging to bring each cell to full charge. Overcharge protection of Li-ion cells is also necessary from a safety stand-point as many of the positive electrode materials used, particularly the layered lithium metal oxides such as LiCoO₂ and LiNi_{0.8}Co_{0.15}Al_{0.05}O₂. decompose to initiate thermal runaway reactions if they are charged beyond a safe voltage limit. In commercial Li-ion battery packs, electronic circuitry is used for overcharge protection and capacity balancing of individual cells as we mentioned in chapter 1. The limitations of external voltage regulation through electronic-circuitry can be overcome with the use of redox shuttle reagents.⁽¹⁾ They are materials with reversible redox potentials slightly above that of the cathode.

If a cell experiences overcharge during charging, the redox reagent, dissolved in the electrolyte, will lock the cell's charge voltage at its oxidation potential. Their chemistry has been described previously.^(2, 3) Many studies dealing with redox shuttle reagents for Li-ion batteries have recently appeared.⁽⁴⁻⁷⁾

2.2. Experimental

2.2.1. Chemical Reagents

Ferrocene (Fc), Diacetylferrocene (DAFc) and Dimethylaminomethylferrocene (DMAMFc) was purchased from Sigma Aldrich, Saint Louis, MO.Acetylferrocene (AFc), Dimethylferrocene (DMFc) and Bromoferrocene (BFc) was obtained from Alfa Aesar, Ward Hill, MA. Ethylene Carbonate (EC), Ethyl Methyl Carbonate (EMC) and lithium hexafluorophosphate (LiPF₆) (battery grade, >99.9 %, H₂O <20 ppm) was purchased from Ferro Corporation, Cleveland, OH. All reagents were electrochemical grade unless mentioned otherwise. All materials were used as received and handled in an Argon-filled Glove Box (MBraun Inc.) in which water level was kept below 5 ppm.

2.2.2. Instrumentation

A computer controlled Auto-Lab (Eco Chemie Inc., model- AutoLab PGSTAT30) potentiostat was used for electrochemical experiments. The electrochemical cell consisted of a traditional 3-electrode system with a Li/Li⁺ reference electrode, a platinum wire counter electrode and a 5mm diameter glassy carbon disc working electrode. The glassy carbon electrode was polished using a 5 μ m alumina paste and followed by cleaning in an ultrasonic water bath prior to each experiment. For the RDE experiments, an analytical rotator (Pine Instruments) was used to rotate the glassy carbon working electrode. The temperature of the experiments was 22±2 0 C.

The test solutions typically contained 3.3mM of each derivative in a 1M LiPF₆/1:1 (by volume) EC:EMC electrolyte. To determine viscosities of the electrolytes, an Ubbelohde Viscometer (size 1) was used. For these experiments, the ASTM (American Society for Testing Materials) protocol was followed as described by the manufacturer. The solution viscosities were measured at 22.5 ± 1 ⁰C by placing the viscometer into a temperature controlled water bath.

2.3.Results and Discussion

We have used a combination of cyclic voltammetry (CV) and rotating disk electrode (RDE) to determine the role of electron withdrawing and donating substituents on the electrochemistry of redox reagents for chemical overcharge protection of rechargeable Li batteries. In particular, we have determined the relationship between heterogeneous reaction rate constants and the Hammett substituent constants, providing information on how the electronic properties of a substituent on a redox reagent affects the rates of redox reactions. This information is supplemented with the determination of a relationship between the Hammett substituent constant and the exchange current densities of the redox reactions of the same reagent. The relevant data was obtained in two steps. First we determined from CV how the Hammett substituent constants influence the redox potentials of the various ferrocenes, and using this information together with the RDE data we have made a quantitative assessment of how an electron withdrawing and an electron donating substituent can affect exchange current density and the electrochemical reaction rate constants.

2.3.1. Ferrocene Substituent Effect and Redox Potentials

The redox reactions of ferrocene and its five derivatives, acetyl ferrocene (AcFc), diacetylferrocene (DAcFc), bromoferrocene (BrFc), dimethyl ferrocene (DMFc) and dimethyl aminoferrocene (DMAMFc), shown Table 1, were studied using cyclic voltammetry (CV) as shown in figure 1A. Sweep rates between 5mv/s and 500mV/s did not change the peak potentials. Examples of AcFc in figure 1B illustrate this. Electrochemical parameters determined from the CV results are compiled in Table 2. The peak potentials of ferrocene depend on the substituent, as noted by others.^(8, 9) The effect of electron donating and withdrawing substituents on peak potentials is readily seen in Figure 1A. The redox potentials of the central Fe atom are shifted either more or less relative to ferrocene by the withdrawing or donating properties of the substituents. Higher oxidation potentials are observed as the electron withdrawing character of the derivative increases. The oxidation and reduction peak potential separation of each material, as seen in Table 2, is in agreement with the theoretical value of 59 mV for one electron reaction. Except for DMAMFc, all derivatives gave one reversible peak. The behavior of DMAMFc is currently under investigation. The unexplained peaks are both time and solvent dependent with only the redox peaks at higher potentials appearing after storing the solution for two days at room temperature. Preliminary data indicate that the higher redox peaks are due to complex, DMAM(Li⁺)Fc, obtained by the acid-base reaction between the aminomethyl group and Li⁺.



 Table 1: Ferrocene and its derivatives studied in this paper



Figure1. (A) Cyclic Voltammograms for 3.3mM ferrocene derivatives in 1M $\text{LiPF}_6/1:1$ EC:EMC on a glassy carbon working electrode at a scan rate of 50mV/s. (B) Cyclic voltammogram for AcFc at sweep rates from 5mV/s to 500mV/s.

To quantify electron transfer we applied the general relationship for reversible reactions shown in equation 1;

$$E_p - E_{p/2} = 2.2 \left(\frac{RT}{nF}\right)$$
 (1)

Where $E_{p/2}$ denotes the half-peak potential, E_p is the peak potential, F is Faraday's constant, and n is the number of moles of electrons involved in the reaction. As seen in Table 2, n is very close to 1 in each of the redox reactions.

Molecule	E _{pa} ±0.002V	E _{pc} ±0.002V	ΔE _p (V)	Number of e ⁻ , n
AcetylFc	3.542	3.480	0.062	0.983
BromoFc	3.452	3.388	0.064	0.983
DiacetylFc	3.773	3.713	0.060	1.001
DMAM ^{Li+} Fc	3.493	3.430	0.063	0.966
DimethylFc	3.167	3.111	0.056	1.057
Ferrocene	3.272	3.213	0.059	1.077

Table 2: Some electrochemical parameters of ferrocene derivatives calculated from cyclic

 voltammograms at 50mV/s scan rate.

We also analyzed the CV data utilizing the Randles-Sevcik relation in equation 2 to obtain diffusion coefficients for the neutral and oxidized species, and for a cross-check of the values of n determined from equation 1.

$$I_{pa} = (2.69 \text{ x} 10^5) \text{n}^{3/2} \text{AD}^{1/2} \text{v}^{1/2} \text{C}$$
(2)

In equation 2, I_{pa} is the anodic peak current, n is the number of electrons transferred during the reaction, C is the concentration of redox reagent, A is the electrode area, v is the scan rate, and D

is the diffusion coefficient of the relevant species. Figure 2 displays Randles-Sevcik plots of BrFc and AcFc which represent the general behavior of all derivatives.



Figure 2. (A) Randles-Sevcik plots of peak currents versus square root of the scan rate for BrFc and (B) for AcFc.

The linearity of the plots of I_{pa} vs. $v^{1/2}$ from CVs collected at sweep rates between 5mV/s and 500 mV/s suggests a diffusion controlled reaction. The diffusion coefficients calculated for all of the ferrocenes are listed in Table 3.

Molecules	D _{ox} (neutral)[technique] X10 ⁻⁶ cm ² /s	D _{red (cation)} [technique] X10 ⁻⁶ cm ² /s	Rate constant,k, (cm/s) [RDE- 2500rpm 10mV, scan rate]	Rate constants,k, (cm/s) [CV, 10mV scan rate)	Radius (nm) (Stokes- Einstein)	Exchange current densities (A/cm ²)
Fc	2.924 [CV] 2.675 [RDE]	2.523 [CV]	1.013x10 ⁻³	8.484x10 ⁻⁴	0.169 [CV] 0.176 [RDE]	7.906x10 ⁻⁶
AFc	2.799 [CV] 1.848 [RDE]	1.790 [CV]	7.995x10 ⁻⁴	7.195x10 ⁻⁴	0.174 [CV] 0.266[RDE]	1.161x10 ⁻⁶
DAFc	2.266 [CV] 1.519 [RDE]	1.621 [CV]	7.048x10 ⁻⁴	6.429x10 ⁻⁴	0.212 [CV] 0.324 [RDE]	8.830x10 ⁻⁸
BFc	4.678 [CV] 3.026 [RDE]	3.275 [CV]	1.119x10 ⁻³	9.585x10 ⁻⁴	0.105 [CV] 0.163 [RDE]	7.031x10 ⁻⁶
DMAM ^{Li+} Fc	2.363 [CV] 1.693[RDE]	1.427 [CV]	7.363x10 ⁻⁴	6.982x10 ⁻⁴	0.203 [CV] 0.284[RDE]	4.364x10 ⁻⁸
DMFc	2.989 [CV] 2.274 [RDE]	2.929 [CV]	9.001x10 ⁻⁴	7.742x10 ⁻⁴	0.161 [CV] 0.212 [RDE]	2.535x10 ⁻⁵

Table 3. Kinetic parameters for ferrocene derivatives determined from CV and RDE data.

In addition, our experimental Randles-Sevcik plots are well-matched with the theoretical plots for n=1. The various electrochemical data indicate that all ferrocene derivatives behave as Nernstian couples in this highly concentrated non-aqueous media. Furthermore, one can easily see from Table 3 that all of the neutral species have higher diffusion coefficients than the oxidized (cation) species. This suggests that the ferrocene cations formed from oxidation

probably ion pair with the $[PF_6]$ anion and solvent as well to form $[Fc^+--PF_6]$ ion pair which diffuse slower than the neutral ferrocenes.

Having determined the diffusion coefficients, we calculated the hydrodynamic radius of each ferrocene using the Stokes-Einstein equation;

$$D = \frac{kT}{6\pi\eta\alpha}$$
(3)

Here, k is the Boltzmann constant, T is the temperature, η is the dynamic viscosity, and α is the effective hydrodynamic radius of the redox molecule. The dynamic viscosity of each material was calculated from the product of the experimentally determined kinematic viscosity and density (1.26 ±0.01 g/cm³), which is 0.045 ±0.001 g/cm.s for all derivatives studied in this work. The calculated radius of each ferrocene is shown in Table 3.

2.3.2. The Electronic Effect of Substituents on the Heterogeneous Electron Transfer

We have determined additional kinetic parameters such as Tafel slopes and exchange currents of the various ferrocenes using rotating disc electrode voltammetry. From this data, the contributions of the various substituents on the heterogeneous rate constants (k) and their relationships to the Hammett substituent constants (σ) were established. The RDE voltammetry is governed by solution convection leading to limiting currents for the electrode reaction, which gives reliable and precise kinetic parameters. Typical RDE data are shown in figure 3 which relates the limiting current, I_{lim} , for the oxidation of a ferrocene to the angular frequency, ω of rotation of the disk working electrode. The data were analyzed using the Levich relationship which expresses the limiting current in terms of the angular frequency of rotation (ω) of the electrode (equation 4).

$$I_{\rm lim} = (0.620) \rm{nFAD}^{2/3} \omega^{1/2} \upsilon^{-1/6} \rm{C}$$
(4)

Where I_{lim} is the limiting anodic current (A), ω is the angular frequency (2 π f/60), and υ is the kinematic viscosity of the electrolyte.



Figure 3. RDE results obtained in 1M LiPF₆/ 1:1 EC:EMC at room temperature on a glassy carbon electrode at 2500 rpm and 10mV/s.

As seen in Table 3,the diffusion coefficients determined from RDE data are slightly lower than those obtained from the CV results, but we consider the results from RDE to be more precise since the mode of mass transport of the electro active species to the electrode surface is through convection which is more efficient. We also plotted I_{lim} vs. $\omega^{1/2}$ to observe the coherency of n (number of electrons) with respect to theoretical n= 1 and that calculated from equation 1. The Levich plots in Figure 4 for DMFc and DAcFc, given as examples, displays straight lines which pass through the origin for all derivatives confirming that the RDE data were obtained under mass transport limited conditions. The results confirm the one electron redox process for all ferrocenes.



Figure 4.Levich plots of I_{lim} currents against square root of rotation speeds at scan rate for DMFc (A) and DAFc (B).

Besides the kinetic parameters discussed above, we also determined from Tafel data the effect of substituents on the exchange current densities (i_0) and heterogeneous rate constants (k). The Tafel equation is a useful method to address the relationship between the rate of an electrochemical reaction vs. overpotential (η). Details of the calculation can be obtained from our previous work.⁽⁶⁾ The plots of logarithmic current versus overpotential of each derivative are displayed in figure 5.



Figure 5. Tafel Plots for oxidation of ferrocene derivatives at room temperature on a glassy carbon working electrode at 2500 rpm for anodic sweep at 10mV/s.

All Tafel plots were based on the mixed kinetic and mass transport anodic region of the RDE voltammograms at 2500 rpm. The open circuit voltage (OCV) was used to define the zero overpotential. Kinetic parameters obtained from these Tafel plots are compiled in Table 3. We found the transfer coefficients (α) to be equal to 0.45 for all ferrocene derivatives, in agreement with literature.⁽¹⁰⁾ The slightly lower transfer coefficient for the oxidized ferrocenes was

attributed to the interactions between oxidized species (cations) and $[PF_6]^-$ as mentioned earlier. We used equation 5 to determine the heterogeneous rate constant (k) for further analysis⁽¹¹⁾;

$$\log I = \log nFACK + \frac{(1-\alpha)nF\left(E-E_{\frac{1}{2}}\right)}{2.3RT}$$
(5)

In equation 5, E denotes the standard potentials, K is the charge-transfer rate constant (cm/s) and the other symbols have their usual meaning described previously. The heterogeneous reaction rate constants are given in Table 3.

2.4. Tuning the Oxidation Potentials of Redox Shuttles

A plot of the potential shift versus Hammett's substituent constant, σ , described by the Hammett Equation is a good way to elucidate the effect of substituent. A Linear free energy relationship provides a quantitative assessment of relationship between structure and its reactivity. The reaction rate or equilibrium between the products of their reaction can change by substitution on the molecule. To elucidate the underlying kinetic mechanism, the Hammett relationship is one of the most useful guiding principles. A relationship between rate and equilibrium constants for ionization of benzoic acid was established by Hammett⁽¹²⁾ according to;

$$k = K^{\rho}G$$
 (6a)

$$logk = \rho logK + logG$$
 (6b)

$$logk = \rho logK + C$$
 (6c)

in which k and K are rate and equilibrium constants, respectively, and C, which is a logarithmic function of G, is a constant, and ρ is a constant as noted in equation 6c. Hammett applied both substituted and unsubstituted benzoic acid's rate and equilibrium constants to equation 6c;

$$\log k - \log k_{\rm H} = \rho \left(\log K \cdot \log K_{\rm H} \right) \tag{7}$$

in which H signifies unsubstituted benzoic acid's either rate or equilibrium constants and calculated Hammett substituent constant $-\sigma$. The latter is defined by the differences between ionization constants of substituted benzoic acid and benzoic acid itself as we can see from equation 7. Using the ionization constants of benzoic acid as a standard reaction, Hammett articulated this relationship, shown in equation 7, in the form of:

$$\log (k/k_{\rm H}) = \rho.\sigma \tag{8}$$

In early studies ⁽¹²⁻¹⁴⁾ sigma (σ) values were documented through the thermodynamic knowledge of unsubstituted ionization constants and substituted ionization constants of benzoic acid. Hammett proposed this equation (8) to determine how substituents on the aryl ring of benzoic acid influence its ionization constants.⁽¹²⁾ Thereafter, it was shown that the Hammett equation could be applied not only to benzene derivatives but also other ring compounds ^(3, 8, 9, 15). Later on, the Hammett relationship was studied via a chronopotentiometric method as well ^(8, 9, 15).

In order to establish a relationship between heterogeneous (electrochemical) reaction and Hammett constants (σ), first, we used the relationship, seen in equation 9, to determine the linearity of potential differences with respect to ferrocene (D_E) as a function of peak potentials. D_E is known as the electrochemical substituent constant⁽⁸⁾

$$D_{E} = E_{ox}[FcX] - E_{ox}[FcH]$$
(9)

Here $E_{ox}[FcX]$ is the oxidation potential of substituted ferrocene and $E_{ox}[FcH]$ denotes oxidation potential of ferrocene itself. The plot D_E vs. peak potentials is seen in Figure 6.



Figure 6. Potential differences of derivatives with respect to ferrocene as function of peak potentials.

Using these D_E values, we calculated Hammett constants from our CV data with the aid of equation 10 proposed by M.Emilia and co-workers⁽⁸⁾ for estimating Hammett constants;

$$D_{\rm E} = 0.031 + 0.473\sigma \tag{10}$$

This relation in equation (10) was derived from experiments in which $[NBu_4][BF_4]$ employed as a salt with tetrohydrofuran (THF) and validated in other aprotic solvents, such as dichloromethane (CH₂Cl₂) and acetonitrile (NCMe) where their⁽⁸⁾ electrolyte compositions were not relevant to lithium battery applications. Therefore in this study this relationship is used to demonstrate its applicability for lithium battery applications. Emilia et al. obtained equation 10 from the slope of plot of known Hammett constants as a function of D_E. They observed that equation 10 was fairly consistent for different redox potentials observed in different solvents based on cyclic voltammetry studies. Ultimately, they reached the conclusion that this equation could be used for estimation of unknown Hammett constants⁽⁸⁾. Therefore, we decided to use this relation to find Hammett constants (σ) from our CV data in EC:EMC-LiPF₆. Our CV-derived Hammett constants as a function of peak potentials are plotted in Figure 7.



Figure 7. CV- based Hammett Constants as a function of peak potentials.

It is clearly seen here that due to strong electron withdrawing characteristics of the acetyl ferrocene derivatives and DMAMLi⁺Fc, they possess larger Hammett constants than those possessing less electron withdrawing or electron donating characteristics. The dimethyl (DMFc) substituent yielded a negative Hammett constant, characteristic of electron donation. Moreover, Hammett constants we observed are consistent with the literature data⁽¹³⁾ which were obtained from ionization of substituted benzoic acid derivatives in water at 25^oC. Hall et al. also found similar values from a chronopotentiometric method to evaluate substituent effects of ferrocene in

NaClO₄ salt dissolved in acetonitrile at 25° C.⁽¹⁶⁾ To the best of our knowledge, this is the first time that the Hammett constants have been determined for ferrocenes in organic carbonate electrolytes and for the Li⁺-complexed DMAMLi⁺Fc derivative in any electrolyte. For the DMAM substituent, one can surmise that the Hammett constant should be close to the DM substituent since DMAM is bonded to the Fc ring through a methylene group. This is confirmed by CV since the oxidation peak potential corresponding to DMAM (3.26 V) was close to that offor DM group (3.19 V) as can be seen in Figure 8.We also found that the Hammett constants corresponding to DAFc is twice that of AFc. This behavior suggests that the substituent effect is additive.



Figure 8. Comparison of cycling behavior of DMFc and initial DMAMFc in 1M LiPF₆ EC:EMC electrolyte at 100mV/s.

The relationship between Hammet constants σ and reaction rate constant can be understood by the relationship as showed previously^(12, 14)

$$\log (k/k_0) = \sigma \rho \quad \text{or} \quad \log k - \log k_0 = \sigma \rho \tag{11}$$

In equation 11, k and k_0 are the reaction rate constants for substituted and unsubstituted ferrocene, respectively, σ is the Hammett constant and ρ is a constant characteristic of the solution. Here we find that this relationship is applicable to heterogeneous reaction rate constants obtained from RDE experiments. In general, free energy is the sum of three type of energy consisting of entropy changes, kinetic energies and potential energies. The first one is not affected by the group conformation reported by H.H. Jaffe in 1953⁽¹⁴⁾. According to Jaffe, Hammett had believed that the entropy and kinetic energy changes are similar and had no effect on substituents. Briefly, free energy differences can be understood as the potential energy differences.

In equation 11, it is necessary to know ρ to fully describe the equation therefore we used the following relationship to obtain rho values (ρ)

$$E_{FcX}-E_{FcH}=\sigma\rho \tag{12}$$

Here, ρ (rho) is a reaction constant, which depends only on the reaction type and a measure of susceptibility of the reaction under the influence of the substituent, and σ is the Hammet substituent constant, described earlier from CV data. Since rho values are solvent dependent, we had to identify appropriate rho values for the derivatives in our electrolyte. More explicitly, rho values rely on both solvent properties, in our case EC: EMC, and the electron donating or electron withdrawing property of the ferrocene substituent. There was no reported rho values used in this medium. Therefore using equation 12 with the known Hammett constants from Figure 7, we found that rho values were around 0.5 for those derivatives possessing electron withdrawing features and -0.367 for DMFc, the only substituent possessing electron

Molecules	Hammett Constants (σ) Based on CV data	Hammett Constants (σ) theoretical	ρ (rho) values based on E _{1/2} -E ⁰ _{1/2} = ρ.σ	Heterogeneous rho (ρ) values divided by -2.3	Heterogeneous Hammett constants (o) Based on RDE data
AFc	0.497	0.502 ¹²	0.535	-0.232	0.443
DAFc	0.987	1.004 ¹⁹	0.504	-0.219	0.719
BFc	0.300	0.232 ¹²	0.580	-0.252	-0.172
DMAM ^{Li+} Fc	0.395	-	0.554	-0.241	0.575
DMFc	-0.294	-0.34 ¹²	-0.367	0.160	-0.321

donating characteristics. Hammett constants determined from equation 11 are compiled in Table 4.

Table 4.Hammett parameters for ferrocene derivatives.

The Hammett plot based on electrochemical reaction rate constants as a function of peak potentials can be seen in Figure 9A. From equations 11 and 12 it is clear that the plot signifies the effect of electron donating or withdrawing property of the substituent on the reaction rate constants of ferrocene derivatives. The trend noticed here is the same as found in Figure 7. This suggests that the heterogeneous rate constants can be applied to the general Hammett equation to obtain heterogeneous Hammett constants with an accurate approximation.

The reaction rate constant, k, increases as the electron donating property of the substituent increases or k decreases as electron withdrawing property increases. This can be clearly understood from Figure 9B. In this plot, the higher Hammett constants signify higher electron withdrawing properties as we discussed earlier of this paper. Derivatives with higher electron withdrawing features manifest lower electrochemical rate constants.



Figure 9.Hammett constants of ferrocene derivatives as function of peak potentials (A) and as a function of electrochemical rate constants (B)

We also determined the trend in exchange current densities as a function of peak potentials and Hammett constants as seen in Figure 10A and 10B, respectively. Here we find the exchange current density increases with increasing electron donating ability of the substituent or it decreases as electron withdrawing property increases. This is not surprising since the exchange current density, a measure of kinetic facility, should be higher as electron density increases at the reaction site. In other words, an electrochemical reaction with a high exchange current density has the rapid kinetics due to faster response to greater electron density. In our study, the highest exchange current density was calculated for DMFc since it was readily oxidized due to greater electron density on the central atom (Fe) than those having electron withdrawing groups.





Figure 10. Exchange current densities based on Tafel data in figure 5 versus peak potentials (A) and as a function of Hammett constants (B).

2.5.References

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CHAPTER 3

THESIS SUMMARY AND FUTURE DIRECTIONS

The electrochemistry of five different ferrocene derivatives has been studied to elucidate substituent effects on the oxidation potentials and reaction kinetics of chemical reagents relevant to overcharge protection of rechargeable Li batteries. A new approach for predicting the substituent effect on redox potentials of chemical shuttles has been developed. We found that higher electron withdrawing substituents provide higher oxidation potentials and electron donating substituents provide lower oxidation potentials. One can estimate the desired potential of redox reagents due to functional group substitution from the plots of Hammett substituent constants versus heterogeneous reaction rate constants and exchange current densities. It is also shown that electron donating and electron withdrawing property of a substituent affect electron transfer rate and exchange current density of electrochemical reactions, obeying a trend opposite to that of theHammett substituent constants (σ).

One of our redox shuttle compounds we have studied, namely DMAMFc, showed two initial CV peaks which we have not been able to fully characterize. The two peaks are both time and solvent dependent with only the redox peaks at higher potentials appearing after storing the solution for two days at room temperature as pointed out in chapter 2. We have assigned this the complex structure, DMAM(Li⁺)Fc, obtained by the acid-base reaction between the aminomethyl group and Li⁺. This material and the observed electrochemistryin non-aqueous electrolytesshould be further investigated by spectroscopic techniques such as NMR.During my Ph.D. studies I am planning to study this material further. Another future direction will be to test the principles developed in this work in new families of redox shuttle reagents for Li-ion batteries.

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Professional Memberships

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Publications

 Electronic Effects of Substituents on Redox Shuttles for Overcharge Protection of Li-ion Batteries, <u>Mehmet Nurullah Ates</u>, Chris J Allen, Sanjeev Mukerjee, K.M. Abraham, *Accepted*, Journal of The Electrochemical Society, (2012)

Oral Presentations at Conferences

 Substituent Effects on the Redox Potentials and Reaction Kinetics of Overcharge Protection Reagents for Li-ion Batteries, <u>Mehmet Nurullah Ates</u>, Chris J Allen, Sanjeev Mukerjee, K.M. Abraham, 220th ECS meeting, October 9-14, 2011, Boston, MA, USA.