

# Deviation from Nernst Equation Predictions in Lithium-ion Battery Electrochemical Potential

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**Abstract**—The Nernst Equation takes into consideration a range of factors in order to accurately determine the electrochemical potential of a battery. In this paper, using an H-Cell and varying concentrations of  $\text{LiPF}_6$  salt dissolved in 1:1 wt Ethyl Carbonate: Diethyl Carbonate Solvent (EC:DEC), the electromotive force (EMF) produced by the incrementing molalities was observed. The experimental data obtained exhibits significant deviations from the values predicted by the Nernst equation as the concentration of the electrolyte increases. The results demonstrate a failure to adhere to the trend predicted by the Nernst Equation, and suggest that in practice solvation effects of lithium ions plays a significant role in the reversible potential of this reaction. The paper discusses the experimental methodology used in determining this effect, results for a common Lithium-ion battery electrolyte, and motivates further investigation into the importance of solvation effects in high concentration electrolytes.

**Keywords:** Li-ion Batteries,  $\text{LiPF}_6$ , Nernst Equation, EMF.

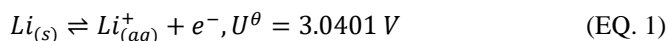
## INTRODUCTION

Lithium ion batteries have proven to be a highly efficient and practical method storing energy in today's world. With a rapid global shift towards renewable energy, as well as the rapid adoption of electric vehicles (EVs) and mobile electronics [1], the demand for these batteries is expected to increase to a yearly growth of 18-20% by 2050 [2]. Thus, there is tremendous ecological and economic motivation to further study and improve these devices.

The primary function of a battery is to store electrical energy in a chemical form and release it as electrical energy when needed [3]. This electrical energy can then be used to power various devices and systems, ranging from small electronic gadgets like smartphones and remote controls to larger applications like electric vehicles and backup power systems. In a typical battery, there are two different types of materials known as electrodes—an anode and a cathode—separated by an electrolyte. When the battery is used to power a device, a chemical reaction takes place between the electrodes and the electrolyte. This reaction allows electrons to flow from the

anode to the cathode, generating an electric current that can be used to do work, such as lighting a bulb or turning a motor [4]. The ability to store and release energy on demand makes batteries extremely versatile and essential in a wide range of applications.

The most common type of battery used today is known as a Lithium-ion battery [5]. In lithium-ion batteries, lithium (Li), a highly reactive element in Group 1 of the periodic table, provides one of the highest electrochemical potentials – this means that as lithium ions react at the cathode, electrons have a high voltage relative to the anode, allowing these batteries to be very energy dense [6]. The electrochemical half reaction of solid lithium to lithium ions (given in Equation 1) and has a reversible potential ( $U^\theta$ ) at standard conditions relative to the standard hydrogen electrode of approximately 3 Volts [7].



These batteries are also highly efficient and reversible [8], due to the “rocking chair” architecture used for almost all Li-ion systems today. The rocking chair architecture refers to the Lithium ions ability to intercalate, or insert itself in the space within crystal lattice, into the anode material (commonly graphite) and the cathode material [9]. This allows for very limited degradation of the anode and cathode material, resulting in higher coulombic efficiency and longer cycle lives [10]. During discharge, Li atoms within the anode release valence electrons that travel to the cathode through an outside circuit, thus producing electricity. Simultaneously, lithium cations migrate through the electrolyte to the cathode, where they intercalate with layers to balance the charge. Recharging reverses the process, and this cycle repeats during battery use.

When studying or designing these batteries, it is important to be able to calculate deviations in the reversible electrochemical potential in solutions not at standard conditions. The Nernst Equation does this by calculating deviations due to changing

pressures, temperatures and concentrations [11]. Assuming that the only redox reaction that takes place is the exchange of Lithium's valence electrons given in equation 1, the Nernst relation for Li is given by Equation 2:

$$E = E^\circ + 2.303 \frac{RT}{F} \log [C_{Li^+}/C_{Li^+,ref}] \quad (\text{EQ. 2})$$

Where,

$E^\circ$  is the standard electrode potential

R is the gas constant

T is the temperature in Kelvin

F is Faraday's constant

$C_{Li^+}$  is the concentration of Li ions in the electrolyte

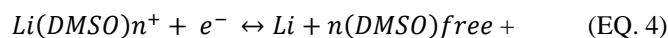
$C_{Li^+,ref}$  is the concentration of Li ions in the reference electrolyte

The Nernst Equation predicts that as the concentration of electrolytes increases, the cell should demonstrate a logarithmic rise in its voltage. In the experimental setup used in this study (outlined in further detail below), the voltage difference between solid lithium electrodes in two Li solutions of different lithium concentrations is measured. The difference in voltage between the two lithium electrodes then is due to the different solution concentrations, so the electromotive force (EMF) applied to the electrons can be summarized as just the difference in the concentration terms in the Nernst equation – this relationship is given by Equation 3.

$$EMF = 2.303 \frac{RT}{F} \log [C_{Li^+,x}/C_{Li^+,ref}] \quad (\text{EQ. 3})$$

Interestingly, Kottam et al. [5] demonstrated that high concentrations of LiTFSI in DMSO does not follow the Nernst equation for standard stripping and plating of Lithium (as given by equation 1).

One possible explanation for the behavior, initially proposed by Kottam et al., is that at high concentrations of Lithium in the electrolyte, the solvating species, must also be considered when deriving the Nernst Equation. The alternative chemical equilibria at high lithium concentrations would therefore be the following.



This is adjustment partially due to the fact that solvent molarities in organic solvents are typically lower than for aqueous system due to the high molecular weight of the solvent species. As Lithium concentration in the electrolyte increases, it therefore much more quickly approaches parity with the solvent. The solvation number of the lithium ions is reduced until a solubility limit is reached.

$$EMF = 2.303 \frac{RT}{F} \left( \log \frac{C_{Li(EC:DEC)n^+(in\ x\ M)}}{C_{(EC:DEC)free^n\ (in\ x\ M)}} - \log \frac{C_{Li(EC:DEC)n^+(in\ ref\ M)}}{C_{(EC:DEC)free^n\ (in\ ref\ M)}} \right) \quad (\text{EQ.5})$$

However, the electrolyte used by Kottam et al. is not typical in modern Li-Ion batteries. In this paper, similar measurements

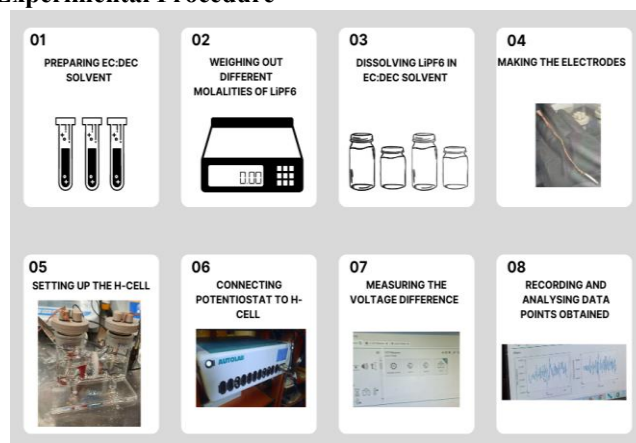
of the EMF were taken for varying concentrations of LiPF<sub>6</sub> dissolved in Ethyl Carbonate: Diethyl Carbonate (EC:DEC), which is a more widely use electrolyte, to determine if this solvation effect is present in modern Li-ion batteries, and to what extent it may play a role in battery operation.

Solvation shells are shells or layers formed by the solvent molecules (EC:DEC) around the solute particles (LiPF<sub>6</sub>) [12]. Solvent molecules interact with ions through a combination of electrostatic forces and Van der Waals interactions. The orientation and alignment of solvent molecules around ions are determined by the balance between these attractive and repulsive forces.

Solvent molecules tend to align their dipoles in response to the charge of the ions, creating an organized solvation structure. Solvation shells can therefore provide a more favorable environment for charge transfer processes at the electrode. Moreover, solvation shells can also lower the activation energy for reactions. The solvation layers can shield the ion from direct interactions with the electrode. This reduces the energetic cost associated with overcoming the electrostatic repulsion between the ion and the electrode [13]. This reduction in activation energy promotes faster charge transfer as cited by Kottam et al. [5].

## METHOD:

### Experimental Procedure



**Figure 1: Schematic depiction of the procedure followed during the experiment**

We prepared a solution of EC/DEC in a 1:1 weight ratio, which was then used as a solvent for the LiPF<sub>6</sub> salt solutions at varying concentrations. We made solutions of 0.05, 0.1, 0.2, 0.5, 1.0, 2.0 and 3.0 molality LiPF<sub>6</sub> in 1:1wt EC/DEC in batches of 15g. Later, density measurements of each solution were taken in triplicate (be measuring the weight of 1mL of solution three times), in order to convert from molality to molarity.

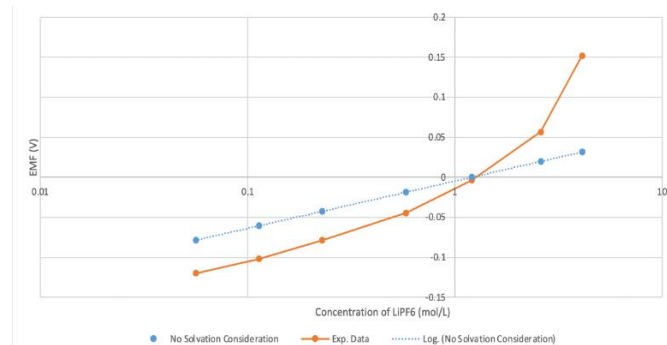
Lithium electrodes were made by wrapping lithium chips around copper mesh strips. The lithium was then brushed to remove any oxide layer that might exist. One electrode was

placed on each half on the H-Cell, a reference solution was added on one side of the H-Cell, and a test solution was added to the other. Measurements were taken first with a 1 molal reference, and then repeated with a 0.2 molal reference for reasons that will be discussed later. An effort was made to minimize the copper mesh contact with the electrolyte. The reference side electrode was connected to the potentiostat counter and reference lines, and the measurement side electrode was connected to the potentiostat working electrode line – in this was the reference electrode was designated to be at 0 V for our measurements, and all open circuit potentials measured are comprised of purely concentration effects.

An open circuit potential between the electrodes was recorded for 20 minutes to allow the system to stabilize, and the final reported EMF is the reading at the end of the measurement time. The voltage differences were then plotted in a graph and the results were analyzed.

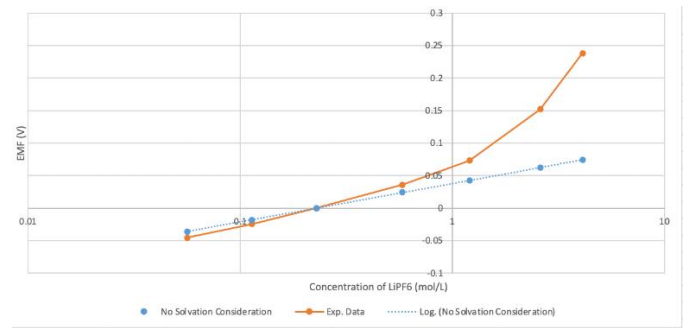
**RESULTS AND DISCUSSIONS**

Initial testing using a 1 molal reference showed significant deviations from the expected Nernst relation at both high and low concentrations. These results are shown in Figure 2, the molarity of the LiPF<sub>6</sub> salt in the electrolyte (in moles per liter) is plotted against the EMF, electromotive force (in Volts), which acts as a measure of the electrochemical potential. The blue line shows the predictions of the Nernst Equation while the red line represents the actual experimental data obtained. At concentrations lower than 1 molal, the experimental results showed a larger than expected EMF depression, and at concentrations higher than 1 molal, the experimental results showed a larger than expected EMF elevation. The authors believe that this result is due to a poor selection of a reference solution. The 1 molal solution was initially chosen because standard electrode potentials are often reported relative to 1 molar electrolyte conditions [7] – however it is believed that at a 1 molal concentration there are already significant solvation effects [14]. A non-ideal reference solution explains the skewed results, and an identical set of measurements using a lower concentration reference solution (0.2 molal) was conducted to limit impact of solvation effects on the voltage measurements at the reference electrode.



**Figure 2: Comparison of theoretical and experimental data with 1 M solution**

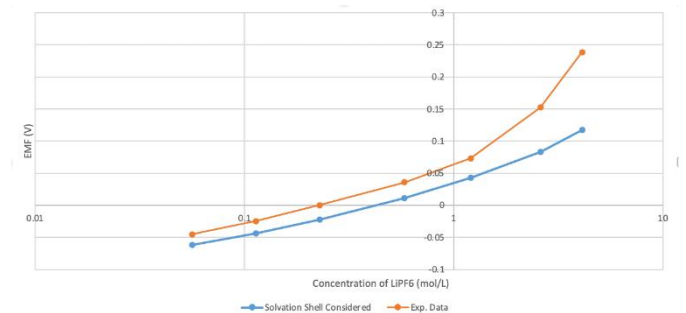
Figure 3 illustrates the results obtained for the 0.2 molal solution. The blue line in the figure represents the predictions of the Nernst Equation while the red line represents the actual data obtained. As can be observed from the plot, the behavior of the electrochemical system exhibits unexpected characteristics at higher concentrations of the electrolyte. Specifically, at lower concentrations, the Nernstian potential closely aligns with theoretical predictions, following a linear trend, whereas, at higher concentrations, an exponential increase in EMF is observed.



**Figure 3: Comparison of theoretical and experimental data with 0.2 M solution**

An inclusion of the electrolyte concentration against the reference concentration yields results that accurately represent the values observed in the experiment suggesting that the consideration of this variable into the formula is necessary.

Figure 4 takes into account the revised formula. The blue line in the figure represents EMF values obtained using Equation 5, while the red line represents the experimental data obtained. The solvation number used for both EC and DEC is 5.84 as per literature values [15] and decreases as the concentration increases. Assuming, the solvation number decreases to 2 at 3M, it is evident that a degree of discrepancy exists between the blue and red lines. However, this may also arise due to experimental inaccuracy and unknown variables. It is important to note, however, that the trend followed by the blue line mirrors that of the red line in the event of higher concentrations being used. Thus, this revised Nernst Equation, more closely follows the trends than the previously used conventional formula.



**Figure 4: Consideration of solvation shells in 0.2M solution**

## CONCLUSION

In this work, we measured the EMF resulting from changing lithium salt concentration in a widely used lithium ion battery electrolyte. Notable differences from theoretical prediction by the Nernst relationship were observed, but only at higher concentrations. This supports the results originally reported by Kottam et al. but with a more practical electrolyte. This suggests that solvation effects do in fact play a large part in Li-ion open circuit potentials, and should be more carefully considered when studying higher concentration systems. Furthermore, both initial result with the 1 molal reference electrolyte, and later results with the 0.2 molal reference electrolyte, show that these effects are already impactful for 1 molal electrolytes, which is well within the concentration range used in typical Li-ion batteries today. This result suggests that this phenomena, which is not widely reported in literature, may be impacting battery performance in a way that is not typically considered by most researchers. Altogether, this study motivates further research into the behavior of lithium salts when stripping or plating from pure lithium, and it demonstrates the continued need to study the basic characteristics of the electrolytes used in today's batteries.

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