



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

M. Nurullah Ates,* Chris J. Allen,* Sanjeev Mukerjee,** and K. M. Abraham***,z

Department of Chemistry and Chemical Biology, Northeastern University Center for Renewable Energy Technology (NUCRET), Northeastern University, Boston, Massachusetts 02115, USA

The redox behavior and kinetic parameters of five ferrocene derivatives were investigated in 1M LiPF₆ in 50:50 volume percent EC:EMC, a typical electrolyte used in lithium-ion batteries. Using cyclic voltammetry (CV) and rotating disk 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. 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 property 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.

© 2012 The Electrochemical Society. [DOI: 10.1149/2.064207jes] All rights reserved.

Manuscript submitted March 6, 2012; revised manuscript received April 12, 2012. Published July 17, 2012. This was Paper 418 presented at the Boston, Massachusetts, Meeting of the Society, October 9–14, 2011.

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 series-connected 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 runaway 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 by releasing oxygen 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. However, electronic circuitry is complex, especially for very large battery packs, and it adds significant cost to the battery. 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

Bis-cyclopentadienyl iron (II) or more commonly known as ferrocene (Fc) is a standard redox reagent⁶ recommended by International Union of Pure and Applied Chemistry (IUPAC)⁸ 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.^{9,10} 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.¹ and later by Golovin et al.³ 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.¹ 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.

In this paper, 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^{12,13} 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 disk 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.

Experimental

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.

*Electrochemical Society Student Member.

**Electrochemical Society Active Member.

***Electrochemical Society Fellow.

^zE-mail: kmabraham@comcast.net