

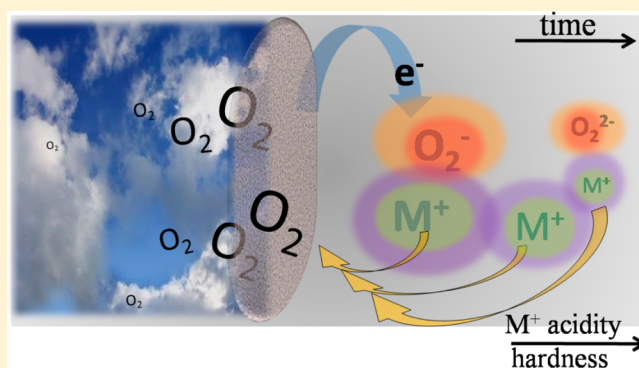
Oxygen Reduction Reactions in Ionic Liquids and the Formulation of a General ORR Mechanism for Li–Air Batteries

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ABSTRACT: Oxygen reduction and evolution reactions (ORRs and OERs) have been studied in ionic liquids containing singly charged cations having a range of ionic radii, or charge densities. Specifically, ORR and OER mechanisms were studied using cyclic and rotating disk electrode voltammetry in the neat ionic liquids (ILs), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) and 1-methyl-1-butyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR₁₄TFSI), and in their solutions containing LiTFSI, NaPF₆, KPF₆, and tetrabutylammonium hexafluorophosphate (TBAPF₆). A strong correlation was found between the ORR products and the ionic charge density, including those of the ionic liquids. The observed trend is explained in terms of the Lewis acidity of the cation present in the electrolyte using an acidity scale created from ¹³C NMR chemical shifts and spin–lattice relaxation (*T*₁) times of ¹³C=O in solutions of these charged ions in propylene carbonate (PC). The ionic liquids lie in a continuum of a cascading Lewis acidity scale with respect to the charge density of alkali metal, IL, and TBA cations with the result that the ORR products in ionic liquids and in organic electrolytes containing any conducting cations can be predicted on the basis of a general theory based on the hard soft acid base (HSAB) concept.



INTRODUCTION

Lithium-ion (Li-ion) batteries have an undeniable influence over our daily lives. Vested in this battery technology are mobile electronics, load-leveling infrastructures, and electric propulsion vehicles. Despite their ubiquity, limits on energy density and the high cost of commercialized Li-ion batteries have accelerated efforts for alternative rechargeable battery systems, such as the nonaqueous Li–O₂ battery, first realized 15 years ago.¹ The 5280 Wh/kg theoretical energy density of Li–O₂ is 7–8 times that of today's best Li-ion battery, and it offers a long-term solution to energy independence.

A primary concern facing this power source is the inefficient rechargeability of insoluble Li_xO_y discharge products that accumulate on the O₂ electrode.² This leads to poor cell performance, stemming from large cathode impedances and the associated voltage gaps between oxygen reduction reactions (ORRs) and oxygen evolution reactions (OERs).^{3,4} Our recent work on the mechanism of ORRs in nonaqueous electrolytes has revealed that the properties of the organic solvent play a significant role in the nature of the final reduction product formed, and the stability of the intermediates through which the conversion of O₂ to Li₂O occurs in the discharge of a Li–O₂ cell. We have gained this insight from a detailed study of the ORR intermediates and products in a series of organic

electrolytes^{5,6} judiciously selected on the basis of their Lewis acid–base properties as defined by Guttmann donor and acceptor numbers. The Guttmann donor number (DN) measures the electron-donating capacity of the solvent to form complexes with Lewis acids such as Li⁺.

Ionic liquids as a class of electrolytes for Li batteries offer several potential advantages over traditional nonaqueous organic solvents. Besides a negligible vapor pressure, high ionic conductivity, and nonflammability, they can be designed to offer enhanced hydrophobicity and large electrochemical stability windows that are highly desirable for their use in the Li–air battery. In this work, we have studied oxygen reduction and evolution reactions (ORRs and OERs, respectively) in two ionic liquids (ILs), namely, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI), and 1-methyl-1-butyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR₁₄TFSI). The PYR₁₄ cation is abbreviated as PYR in this report. The cations and common anion of these ionic liquids are shown in Scheme 1.

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