

## Predicting the Electrochemical Behavior of Lithium Nitrite in Aprotic Solvents

V. S. Bryantsev, J. Uddin, V. Giordani, W. Walker,  
G. V. Chase, D. Addison

Liox Power, Inc.

129 N. Hill Ave., Suite 103, Pasadena, CA 91106, USA

Email: [slava@liox.com](mailto:slava@liox.com)

Solvent plays a critical role in determining the nature of discharge products and cycling characteristics of the organic electrolyte rechargeable Li-O<sub>2</sub> battery. One of the biggest challenges is to develop an electrolyte composition that is sufficiently stable to both the Li anode and O<sub>2</sub> cathode environments upon long-term cycling. We have recently reported<sup>1</sup> on the Li-O<sub>2</sub> cell that enables longer duration cycling (>2000 hours) with significantly reduced decomposition of electrolyte materials compared to Li-O<sub>2</sub> cells previously reported in the field. This performance is achieved by combining straight-chain alkyl amides, which are significantly more stable to the reactions of the O<sub>2</sub> electrode than conventional electrolyte solvents,<sup>2</sup> with the lithium nitrate (LiNO<sub>3</sub>) salt, which is capable of stabilizing a solid-electrolyte interphase (SEI) on the Li anode.<sup>3</sup>

A stabilizing effect of LiNO<sub>3</sub> on the Li metal electrode stability can be related to the formation of insoluble Li<sub>2</sub>O according to the following reaction<sup>4</sup>

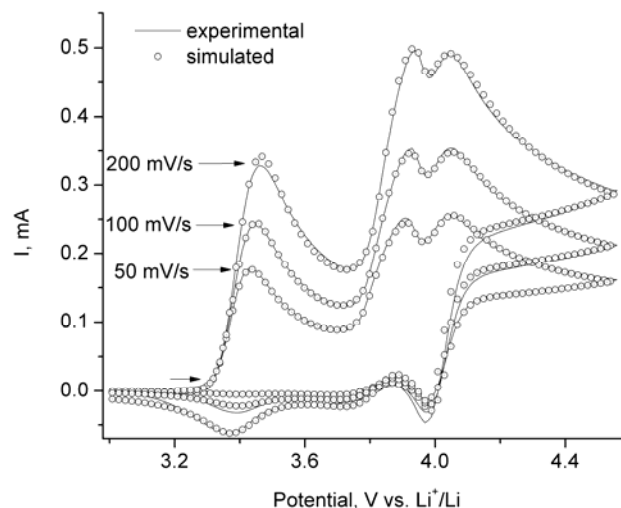


Another product of this reaction, lithium nitrite (LiNO<sub>2</sub>), is an electroactive species in the charge voltage range of a Li-O<sub>2</sub> cell. Small oxidation processes observed<sup>1</sup> at 3.6–3.7 from linear sweep voltammetry and galvanostatic charging of a Li-O<sub>2</sub> cell with a LiNO<sub>3</sub>/N,N-dimethylacetamide (DMA) electrolyte are consistent with the presence of LiNO<sub>2</sub> in an electrolyte solution. Thus, knowledge of the chemical and electrochemical behavior of LiNO<sub>2</sub> in aprotic solvents is essential to provide a more complete picture of electrolyte stability toward both the O<sub>2</sub> electrode and Li anode.

The electrochemical oxidation of the oxygenated nitrogen compounds has been studied previously in various media. However, the reported results are often inconsistent.<sup>5–8</sup> For example, the redox potential of the NO<sub>2</sub>/NO<sub>2</sub><sup>+</sup> couple was reported to vary by more than 0.6 V in the same solvent.<sup>7,8</sup> This ambiguity was assigned to the problem of contamination by traces of water that can react with nitrogen oxides to generate new electroactive species.<sup>7</sup> Due to lack of detailed mechanistic knowledge of nitrite oxidation, there are significant contradictions and variations in the interpretation of the successive oxidation waves of the nitrite anion.<sup>5–7</sup> Quantum chemical calculations can provide a convenient method to elucidate the mechanism of nitrite oxidation in aprotic solvents and guide the assignment of the cyclic voltammetry peaks.

In this work, we employ density functional theory (DFT) and coupled-cluster (CC) calculations to predict redox potentials of oxygenated nitrogen compounds in acetonitrile solution. Acetonitrile is chosen as a solvent in this study because similarly to straight-chain alkyl amides it shows improved stability toward reduced O<sub>2</sub> species,<sup>2</sup> but offers a wider electrochemical window, thus

extending the range of accessible redox potentials. Ion solvation is modeled by explicit inclusion of 8 solvent molecules in the vicinity of the ion and implicit treatment of the rest of the solvent with a dielectric continuum model. This mixed cluster/continuum framework avoids the ambiguities of assigning atomic O and N radii for ionic compounds, because the results are not sensitive to the choice of these parameters if a solute is completely surrounded by solvent molecules. Excellent agreement with the experimental redox potentials provides strong support for the computational model, thereby lending credence to the calculated solvation free energies of various ionic nitrogen–oxygen species. Furthermore, we have investigated the mechanism of the chemical reaction between the nitrite anion and its first oxidation product, nitrogen dioxide (NO<sub>2</sub>). We find that the interconversion between nitrogen dioxide and its various dimers provides a low energy path for the reaction with the nitrite anion. Good agreement between experimental and simulated cyclic voltammograms for electrochemical oxidation of LiNO<sub>2</sub> in acetonitrile (Figure 1) provides support to the proposed mechanism of coupled electrochemical and chemical reactions. The results have important practical consequences for rechargeable Li-O<sub>2</sub> batteries, suggesting a possible mechanism of LiNO<sub>3</sub> regeneration in the electrolyte.



**Figure 1.** Comparison of experimental and simulated voltammograms for the oxidation of 10 mM LiNO<sub>2</sub> in acetonitrile at a Pt working electrode ( $S = 0.196 \text{ cm}^2$ ).

## References

1. W. Walker, V. Giordani, J. Uddin, V. S. Bryantsev, G. V. Chase, D. Addison, *J. Am. Chem. Soc.* **135**, 2076 (2013).
2. V. S. Bryantsev, J. Uddin, V. Giordani, W. Walker, D. Addison, G. V. Chase, *J. Electrochem. Soc.* **160**, A160 (2013).
3. D. Aurbach, E. Pollak, R. Elazari, G. Salitra, C. Kelley, J. Affinito, *J. Electrochem. Soc.* **156**, A694 (2009).
4. J. Poris, I. Raistrick, R. Huggins, *Proc. Electrochem. Soc.* **84-2**, 313 (1984).
5. C. E. Castellano, J.A. Wargon, A. J. Arvia, *J. Electroanal. Chem.* **47**, 371 (1973).
6. G. Bontempelli, G.-A. Mazzocchin, F. Magno, R. Seeber, *J. Electroanal. Chem.* **55**, 101 (1974).
7. A. Boughriet, M. Wartel, *J. Electroanal. Chem.* **362**, 167 (1993).
8. K. Y. Lee, C. Amatore, J. K. Kochi, *J. Phys. Chem.* **95**, 1285 (1991).