Electrochemistry of lithium–oxygen batteries using microelectrode voltammetry

CrossMark

E. Joseph Nemanick*

Energy Technology Department, The Aerospace Corporation, 2310 E. El Segundo Blvd., El Segundo, CA 90245, USA

H I G H L I G H T S

- Microcavity electrodes are a rapid tool for materials characterization.
- Li–O_2 discharge products are distinct species of surface and bulk Li_2O_2.
- Using single walled nanotubes leads to lower charge voltages and higher capacities.

A R T I C L E   I N F O

A B S T R A C T

The electrochemistry of non-aqueous lithium–oxygen (Li–O_2) batteries on both reduction and oxidation was investigated using carbon black and single-walled nanotube (SWNT) microcavity electrodes. Two oxidative peaks were observed on oxidation (charge). The first peak at 3.0–3.7 V vs. Li/Li$^+$ was limited in storable charge ($\sim 8 \times 10^3$ C cm^{-3}). The oxidation potential of this first peak was independent of Li_2O_2 thickness (as measured by total charge on reduction) and assigned to interfacial Li_2O_2, lying between the bulk of the Li_2O_2 and the carbon surface. A second peak between 4.0 and 4.6+ V showed significant discharge product thickness dependence on oxidation potential and was assigned to bulk Li_2O_2, away from the carbon surface. On reduction (discharge), deposition of the interfacial Li_2O_2 showed a significant overpotential indicated by the ratio of interfacial/bulk Li_2O_2 formed at varying reduction potentials. SWNT were shown to effectively decrease the Li–O_2 average charge overpotential for a given charge by increasing the electrode surface area available for formation of interfacial discharge products.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The energy storage capacity of intercalative materials such as layered oxides and carbons has begun to reach their practical limits and will be insufficient for the extended driving range required for mass adoption of electric vehicles as well as advancements in portable electronics [1]. To meet these needs, new battery chemistries are sought using next generation anode materials such as silicon and lithium metal, and group VI cathode materials sulfur [2,3] and oxygen [4,5] being the focus of extensive research. For oxygen, in particular, the reversible two electron reduction of O_2 in the presence of Li$^+$ to form Li_2O_2 in non-aqueous electrolytes has received considerable interest. Estimates for the energy density of practical systems range widely from 800 to 3000 Wh kg^{-1} [6,7], four to fifteen times the energy density of present Li-ion cells. Although this technology has the potential to offer significantly

greater energy storage density than current Li-ion chemistry, there are significant issues related to oxygen electrode chemistry that must be addressed. Such issues as electrolyte breakdown [8], electrode reactivity [18,19], and high reaction overpotentials [9] are areas of intense research. A complete understanding of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) mechanisms in reversible non-aqueous aprotic electrolytes remains elusive.

Recent work [10] has eliminated the previous solvents of choice, alkyl carbonates, as suitable for Li–O_2 due to their decomposition to form Li_2CO_3 with cycling. Analysis of evolved gas using differential electrochemical mass spectrometry, DEMS [11], as well as Fourier transform infrared spectroscopy (FTIR) [12], Raman spectroscopy [13], and nuclear magnetic resonance (NMR) [14] studies have shown that reduced O_2 species react with alkyl carbonates rather than reversibly cycling [15]. Attention has since been focused on etheric solvents [16] such as dimethoxy ethane (glyme) and tetra-glyme which while still showing some oxidative instability at high potentials [17], does reversibly produce Li_2O_2 on the cathode. Reports also indicate that these highly reduced O_2 species may also

* Tel.: +1 (310) 336 0093.
E-mail addresses: ejoseph.nemanick@aero.org, nemanice@gmail.com.

react with the high surface area carbon materials used as electrodes, which may call for investigation of more oxidatively stable high specific surface area materials [18–20].

Understanding the nature of the oxygen reduction reaction (ORR) and oxygen evolution reactions (OER) is fraught with difficulty. Several models have been advanced after the semi-reversible reaction of oxygen with lithium was discovered in etheric solvents [9,21,22]. Many measurements have characterized Li−O$_2$ reaction chemistry using macroscale (>1 mm) electrode cycling and/or rotating disk [9] (or ring disk [23]) measurements. Macroscale measurements give fidelity to end use, but are necessarily slow and can contain many confounding elements. The rotating electrodes eliminate effects from slow diffusion rates and low O$_2$ solubilities at the expense of using representative electrode materials, as they rely on Pt and glassy carbon disks. It is critical to develop techniques to allow for evaluation and elucidation of the fundamental reaction mechanism without other processes such as diffusion, Li anode degradation, and solution impedance and capacitance, while still using end-product relevant electrode materials.

To study the ORR and OER processes, this project has utilized microcavity voltammetry. Microcavity voltammetry uses a pore formed by etching back the wire of a metal microelectrode packed with high surface area electrode material. Microcavity electrodes, like microelectrodes, increase the mass transport of oxygen to the electrode through hemispherical diffusion, but also use the same electrode materials as their macroscale cousins. Microcavity electrodes cannot be strictly modeled using conventional microelectrode equations, for in addition to the hemispherical diffusion of species to and from the cavity opening, there is a diffusion process down the length of the cavity through the porous material, and so acts like a hybrid of micro- and macro-electrodes. Current passing through the small working electrode surface is greatly reduced, decreasing the iR losses associated with the organic electrolyte and increasing the usable scan rates. The small surface area also reduces the capacitive signal of the electrode, allowing the Faradaic signal to be more easily measured. In addition, the small absolute amount of Li$^+$ consumed during cycling allows for the substitution of a non-lithium counter electrode, removing the confounding effects of a highly reactive electrode from the measurements.

2. Experimental

2.1. Preparation of active material

For studies of carbon electrode lithium−oxygen cells, the high surface area carbon electrode was made from Super C65 carbon black (Timcal, BET surface area 62 m^2 g^{-1}), with a particle size distribution between 30−50 nm. In addition, single walled carbon nanotubes (SWNT, 1.4 nm dia., 1/3 conducting:2/3 semiconducting, NanoIntegris, ~1000 m^2 g^{-1}) were also tested as higher surface area materials. Carbon black or SWNT (100 mg) in iso-propanol (5 mL) were sonicated in a MiSonix S-4000 Ultrasonicator at 17 W for 10 min to disperse the carbons. 10% dry weight of T-30 Teflon water-based emulsion (DuPont) was added and the solution was mixed. The iso-propanol and water were then evaporated under an active vacuum. The dried material was then formed into a thick gum by addition of small amounts of i-propanol and thoroughly mixed and folded until the material was uniform. Microcavity electrodes were fabricated adapting a technique from Wang et al. [24]. A 15 μm Pt wire microelectrode (Ametek, Berwyn, PA) was polished flat using 0.1 μm alumina, and then immersed in hot (80 °C) aqua regia for 30 min to etch down the Pt wire and form a microcavity. Active material was then worked into the microcavity by using the electrode as a pestle against a glass surface. The cavity filling was observed by microscope and the excess material

removed by cleaning with a soft cloth. The electrode was then dried in vacuum before use. At the end of experimentation, the active material was removed from the cavity by sonicating in i-propanol and the electrode was freshened by dipping in room temperature aqua regia for <5 s before refilling and reuse.

2.2. Electrochemical measurements

Electrochemical measurements were carried out with either 0.5 M tetrabutylammonium trifluoromethane sulfonate (TBATFS, Aldrich, >99.0%) or 0.5 M lithium trifluoromethane sulfonate (triflate, LiTFS, 99.995%, Aldrich) in diglyme (DG, anhydrous, 99.5% Aldrich, dried over molecular sieves), prepared in an Ar glovebox. Lithium triflate was chosen as the salt due to its slightly better stability on cycling and lower charge voltage plateau than the imide salt, LiTFSI. The reference electrode was a Ag wire, isolated from the working electrode by a Vycor frit, in 10 mM AgNO$_3$/0.5 M LiTFS/DG. The reference electrode was kept ~1 cm from the working electrode. The 10 mM Ag/Ag$^+$ reference electrode was 3.52 V [10] more positive than a Li/Li$^+$ reference, which was not used as the presence of O$_2$ can cause variations in the reference potential of this electrode. For some studies, the LiTFS was replaced with the TBATFS, to examine the chemistry in the absence of Li$^+$. O$_2$ free electrolyte measurements were performed in an Ar glovebox (O$_2$ < 1 ppm, H$_2$O < 1 ppm) with an electrolyte prepared from solvent and salt stored in the glovebox. A three electrode cell was prepared using 20 mL of 500 mM LiTFS or TBATFS in DG in a dried three neck flask with a stainless steel mesh counter electrode (2 × 2 cm). For O$_2$ saturated experiments, the solution was bubbled with O$_2$ (Matheson, 99.997%, passed over a CaSO$_4$ drying column) with vigorous stirring for 1 h. The O$_2$ saturation of the solution was tested by watching for a change in reductive response to vigorous stirring or direct bubbling of O$_2$ over a test electrode surface during a galvanostatic scan. If the current during reduction did not increase, the solution was deemed to be saturated. The potentiostat was a PAR 273A run using Corrware software.

3. Results and discussion

3.1. Microelectrode voltammetry

Typical voltammograms of microelectrodes for a reaction with freely diffusing reactants and products show a profile similar to high rate rotating systems, with the typical peak of macroscale cyclic voltammograms (CVs) being replaced with a steady state saturation current and little reaction hysteresis [25]. For non-aqueous lithium−oxygen chemistry in glymes the solid product Li$_2$O$_2$ formed from the ORR occludes the surface and prevents subsequent reaction reducing the saturation current and eventually terminating the reaction [9,16,21,22]. Fig. 1 shows a CV of 15 μm diameter × 30 μm deep cavity carbon black electrode scanned at 10 mV s^{-1} in (A) O$_2$ free and (B) O$_2$ saturated 0.5 M LiTFS electrolyte in DG. These traces can be compared to the same electrode in (C) O$_2$ saturated, Li$^+$ free, 0.5 M TBATFS/DG. Both O$_2$ saturated samples (with and without Li$^+$) showed the onset for the ORR, starting at ~2.7 V vs. Li/Li$^+$ for the LiTFS and ~2.2 V for TBATFS, demonstrating the stabilization of reduced oxygen species by Li$^+$ in forming Li$_2$O$_2$ [26,27]. The overall reaction of

$$2Li^+ + O_2 + 2e^- \rightarrow Li_2O_2 \text{ (s)} \tag{1}$$

forms an insoluble, poorly conducting product which slowly decreases the active surface area. The electrically insulating nature of the discharge product will retard subsequent reduction. As the thickness of discharge products increases, reduction at the surface