Challenges facing rechargeable lithium-air batteries

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First lithium-water batteries

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Anodic Behavior of Lithium in Aqueous Electrolytes

I. Transient Passivation

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ABSTRACT

Lithium manifests a transient passivation when it is anodically polarized to ~ -2.66 NHE in LiOH electrolytes. The duration of the passivation ranges from seconds to hours. The occurrence of the passivation is independent of electrolyte concentration, flow velocity, anode-cathode contact pressure, and of the polarization technique used. The duration of the transient is proportional to electrolyte concentration, the more dilute the solution the shorter the time. The passivation is believed due to the formation of an insulating, but unstable aggregate of Li₂O which nucleates at active Li sites at the base of the pores in the protective LiOH film. The recovery of the surface to the active state is due to the conversion of the Li₂O to LiOH in the presence of water at the Li surface.

The recent discovery of ways to electrochemically harness the lithium-water reaction (1) has prompted basic studies of the electrochemical reactions of lithium in aqueous electrolytes. Attempts to minimize polarization effects and to attain high current efficiency have been the subject of an ongoing program. Electrochemical characteristics of the lithium-water cell have been treated in a recent paper (2).

The chemistry of the lithium-water reaction is relatively simple, but the electrochemistry of the system is complex because (i) the reaction rate between lithium and water is very fast and the major portion of the lithium electrode is always covered with thick oxide films under anodic polarization, within certain ranges of hydroxyl ion concentration and electrolyte flow, two types of passivation are manifested. First, transient passivation is observed at a specific electrode potential. As is described in this paper, it is apparently related to the formation of an intermediate oxide. Second, actual mechanical passivation occurs and is presented in Part II of this subject title. Part III deals with the influence of electrolyte flow velocity on the surface coverage of the lithium anode.

Experimental

A general setup of the electrochemical cell is shown in Fig. 1. It was designed with the following require-



Demands for Li-ion batteries



Primary energy resources consumption







Efficient turbo-diesel motor

Power 326 h.p.

Engine efficiency $\sim 40 \%$

Tank-to-wheel efficiency:





Motor wheel

Power 80 x 4 = 320 h.p. Motor efficiency > 90 % Battery-to-wheel efficiency:

90 %



Total weight **1500 kg** Battery weight **300 kg** Energy storage **24 kWh** Range **<150 km**



J. Christensen et. al. // J Electrochem Soc 159 (2012)

For **500 km** range we need at least 70 - 80 kWh Battery would weight about **900 kg** !



non-aqueous cathode $O_2 + nLi^+ + ne^- \rightarrow LiO_x$ or aqueous cathode $0.5O_2 + H_2O + 2Li^+ + 2e^- \rightarrow 2LiOH$

Estimations for energy per active components only



J. Christensen et. al. // J Electrochem Soc 159 (2012)

Estimations of practical energy



J. Christensen et. al. // J Electrochem Soc 159 (2012)

Possible high-energy battery chemistries

- Rechargeable lithium-metal-intercalation positive electrode (up to 300 - 400 Wh/kg cell level)
- New generation of high-voltage lithium-ion (up to 300 - 400 Wh/kg cell level)
- Lithium-sulfur (up to 600 Wh/kg cell level)
- Lithium-air (up to 1 000 Wh/kg cell level)



 $Li \rightarrow Li^+ + e^-$

Side reactions: $Li + H_2O \rightarrow LiOH + H_2$ $Li + O_2 \rightarrow Li_2O$

Huge volume changes

$O_2 + nLi^+ + ne^- \rightarrow LiO_x$

Side reactions: $Li_2O_2 + H_2O \rightarrow LiOH + O_2$ $Li_2O_2 + CO_2 \text{ (wet)} \rightarrow Li_2CO_3 + O_2$

Reaction reversibility

Proper oxygen, electron and Li⁺ transport in the electrode

Lithium-oxygen cell PHYSICAL CHEMISTRY Letters designs PERSPECTIVE



pubs.acs.org/JPCL

Challenges associated with metallic lithium anode

Non-uniform lithium plating







Dioxolane - "magic" solvent?



Lithium plating under pressure

C. Monroe & J. Newman // J Electrochem Soc 152 (2005)

2.5 mAh/cm² (about 12 μ m) at C-rate

uniaxial pressure 10 kg/cm²



no pressure

Y.V. Mikhaylik et. al. // ECS Transactions 25 (2010)

Electrolytes for lithium protection



Dendrites in hybrid polymer electrolyte



F. Orsini et. al. // J Power Sources 76 (1998)

NASICON type electrolytes (e.g. Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃)



G.Yu. Aleshin et. al. // Solid State Ionics 184 (2011)





N. Kamaya et. al. // Nature Materials 10 (2011)



N. Kamaya et. al. // Nature Materials 10 (2011)

Solid electrolyte thickness



G.Yu. Aleshin et. al. // Solid State Ionics 184 (2011)





* to get specific energy > 1 kWh/kg

Non-aqueous air cathodes: factors limiting the capacity

First theoretical models





First theoretical models



P.Albertus et al. // J. Electrochem. Soc. 158 (2011)

Specific capacity (mAh/g Super P carbon)

Oxygen diffusion limitations



Oxygen map (EDX) of the electrode discharged (100% DOD) at 0.5 mA/cm²

Non-aqueous air cathodes: materials and electrolytes

First lithium-air battery



100 μm thick Chevron acetylene black electrode 0.1 mA/cm^2

K.Abraham et al. // J. Electrochem. Soc. 143 (1996)

MnO₂ catalysts

Super P carbon + catalyst





A.Debart et al. // Angew. Chem. Int. Ed. 47 (2008)

Microscopic observation of discharge product on CNT



R.R.Mitchell et al. // Ener. Environ. Sci. 4 (2011)

Experimental approaches to probe reaction pathways

- X-ray photoelectron spectroscopy (in situ and ex situ)
- Raman and FTIR spectroscopy (in situ and ex situ)
- Differential electrochemical mass-spectroscopy (in situ)
- X-ray powder diffraction (ex situ)
- Electron microscopy (ex situ)

Side reactions with electrolytes



Freunberger et al. // JACS 133 (2011)

Mechanism of alkylcarbonate decomposition



2 O ₂ ^{•-} + 2 CO ₂	->	$C_2O_6^{2-} + O_2$	(6)
C ₂ O ₆ ²⁻ + O ₂ ⁻ + 4 Li ⁺		2 Li ₂ CO ₃ + 2 O ₂	(7)

Freunberger et al. // JACS 133 (2011)

Possible reaction pathways

discharge $O_2 + Li^+ + e^- = LiO_2 (3.0 V)$ $2LiO_2 = Li_2O_2 + O_2$ $LiO_2 + Li^+ + e^- = Li_2O_2 (3.1 V)$

recharge $Li_2O_2 = O_2 + 2Li^+ + 2e^-$

Laoire et al. // J Phys Chem C I I 3 (2009)

Possible instability of carbon



B. McCloskey et al. // J Phys Chem Lett 3 (2012)

DFT calculations



J. Xiao et. al. // Nano Letters 2011



Carbonate formation on carbon blacks



Z. Peng et al. // Science 337 (2012)



Y. Xu, W.A. Shelton // J Electrochem Soc 158 (2011)

Nanoporous gold as an alternative





up to 5 mg/cm² only 1.5 mAh/cm²

Z. Peng et al. // Science 337 (2012)



Thank you for your attention!

Further reading

- Peter G. Bruce at.al., Li–O₂ and Li–S batteries with high energy storage // Nature Materials II 19-29 (2012)
- Jake Christensen at. al., A Critical Review of Li-Air Batteries // Journal of The Electrochemical Society **I59** (2) RI-R30 (2012)
- Advanced Batteries: Materials Science Aspects by Robert Huggins (2008)
- Linden's Handbook of Batteries, 4th edition by Thomas Reddy (2010)