Modelling of a Na-air battery with porous gas diffusion electrode

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ABSTRACT

A macro-homogeneous model has been developed to evaluate the impact of replacing conventional flooded electrode with gas diffusion electrode on the performance of a novel non-aqueous Na-air battery under pure oxygen gas. After the model has been validated with experimental data, the model results exhibit a significant improvement in battery performance, providing about a 48% increase in initial discharge capacity (over 1551 mAh/g_{carbon} at 0.1 mA/cm^2) and higher discharge potential when using a gas diffusion electrode rather than a flooded electrode. Overall, the gas diffusion electrode model shows the promising performances for a rechargeable Na-air. The model correlates the relationship between the performance and electrolyte decomposition and the formation of discharge products (such as Na_2O_2 and Na_2CO_3). The developed model can be potentially used to optimise electrode structure and electrolyte loading in the active layer, leading to improve the battery performance.

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1. Introduction

Over the last decades many studies have devoted much effort to the rechargeable Lithium-oxygen/air batteries (Li-air) as an advanced energy storage and new electrochemical technology with high theoretical specific energy [1–3]. In contrast to commercial lithium battery systems, the Li-air battery merges the advantage of fuel cell and batteries in that one of the active materials (oxygen or air) comes from the atmospheric air. When assuming lithium peroxide (Li_2O_2) as a solid product, the cell system ideally operates at up to the potential of 2.96 V and exhibits a theoretical specific energy of 3458 Wh/kg several times higher than that of conventional lithium-ion batteries generally applied in commercial electronic devices market or even electric vehicles. However, a major problem with this kind of application is that the large overpotentials have been found in practical cells on discharge ($\eta_{dis} \approx 300$ mV) and on charge ($\eta_{chg} > 1$ V), resulting in low round-trip efficiency about 67% during battery cycling.

Therefore, much effort has been put into the search for suitable catalysts to increase Li-air performance. Despite its safety and efficiency issues, some early results reveal a more complex cell reaction [4–6]. There was strong evidence that the non-aqueous electrolytes applied in Li-air batteries using both carbonate and ether-based solvents tend to react with the intermediate product of reactive superoxide radical (O_2^-) formed during reduction reaction of oxygen [7–9]. This superoxide makes the electrolyte degradation to form solid by-products which are irreversible during the cell discharge and charge cycles. Recent research found that the Li-air operated in ether-based electrolyte can form the desired discharge product of Li_2O_2, but it still suffers from electrolyte degradation and results in large overpotentials [10–12]. Moreover, there is increasing concern that the cost of lithium may rise as demand for battery materials increases [13]. Hence, substitution of lithium by sodium metal, which provides very suitable redox potential as high as lithium ($E^0_{(Na^+/Na)} = -2.71$ V compared to $E^0_{(Li^+/Li)} = -3.05$ V versus standard hydrogen electrode), may offer promising rechargeable metal-air batteries for energy storage application.

Replacing the lithium electrode by the abundant and inexpensive sodium to assemble an analogous Na-oxygen/air cell still maintains an energy storage system with a high specific energy depending on the discharge products, i.e. Na_2O_2 provides 1605 Wh/kg with standard cell potential $E^0 = 2.33$ V. Furthermore, sodium is placed right below lithium in the periodic table and it is expected that their chemical properties could be similar. The working principle of both lithium and sodium oxygen battery systems is similar in concept as shown in Fig. 1. For a non-aqueous electrolyte system, the possible cell reactions during discharge process for Na-air battery are the formation of different sodium oxide products by

Nomenclature

a	Specific interfacial area (m^2/m^3)
A	Membrane surface area (m^2)
c_i	Concentration of species i (mol/m^3)
$c_{i,s}$	Concentration of species i at the wall or surface of electrode (mol/m^3)
D_i	Diffusion coefficient of species i (m^2/s)
$D_{i,eff}$	Effective diffusion coefficient of species i (m^2/s)
D_{ij}	Stefan-Maxwell binary diffusivities (m^2/s)
D_{ij}^{eff}	Effective stefan-Maxwell binary diffusivities (m^2/s)
$\tilde{D}_{ij}$	Symmetric diffusivities (m^2/s)
E	Electrode potential of cathode at any state (V)
E^0	Electrode potential of cathode at standard state (V)
f	Activity coefficient of LiPF$_6$ salt
F	Faraday's constant (96,485 C/mol)
H	Henry's law constant (mol/m^3/atm)
i_0	Exchange current density (A/m^2)
i_1	Current density in the electrode phase (A/m^2)
i_2	Current density in the electrolyte phase (A/m^2)
I	Applied current density (A/m^2)
j_m	Interfacial or local transfer current density of reaction m (A/m^2)
J	Volumetric current density (A/m^3)
$\mathbf{J_i}$	Diffusion flux (kg/m^2/s)
k	Reaction rate constant
l	Thickness of discharged products film (m)
l_e	Thickness of electrolyte film (m)
l_m	Thickness of membrane (m)
L_A, L_C, L	Thickness of APL, separator, and porous cathode respectively (m)
M_i	Symbol for the chemical formula or molecular weight of species (mol/kg)
n	Number of electrons transferred in the electrode reaction
$\mathbf{N_i}$	Molar flux of species i (mol/m^2/s)
$\mathbf{N_{i,mass}}$	Mass flux of species i (kg/m^2/s)
p	Geometrical factor or pressure inlet (Pa)
$\bar{p}$	Partial pressure of gases (Pa)
r_0	Particle radius in the electrode (m)
r_i	Reaction rate term that accounts for electrochemical and chemical reactions (mol/m^3/s)
R	Universal gas constant (8.3143 J/mol/K)
R_{film}	Electrical resistivity across Li$_2$O$_2$ film formation (Ω m^2)
s_i	Stoichiometric coefficient of species i in electrode reaction
S	Electrolyte fraction in the porosity of the electrode
S_{mass}	Source terms (kg/m^3/s)
t	Time (s)
t_+	Transference number of cation in electrolyte
T	Temperature (K)
$\mathbf{u}$	Darcy velocity (m/s)
v_i	Molecular diffusion volumes of species i (m^2)
V_{cell}	Cell voltage (V)
w_i	Mass fraction of species i
x_i	Mole fraction of species i
z_i	Valence of charge number of species i

Greek letters

α	Transfer coefficient
β	Symmetry factor
ε	Porosity or void volume fraction of porous cathode
ε_c	Initial volume fraction of cathode electrode (carbon, catalyst and binder)
ε_g	Volume fraction of gas
ε_l	Volume fraction of liquid electrolyte
ε_s	Volume fraction of solid phase in porous cathode
η	Surface or activated overpotential (V)
κ	Conductivity of electrolyte (S/m)
κ_{eff}	Effective conductivity of electrolyte (S/m)
$\tilde{\kappa}$	Permeability of porous media (m^2)
μ	Viscosity of electrolyte (Pa s or kg/m/s)
μ_i	Pore-fluid viscosity of gas i in GDE (Pa s or kg/m/s)
μ_0	Viscosity of pure solvent (Pa s or kg/m/s)
ν	Number of moles of ions into which a mole of electrolyte dissociates
ν_+	Numbers of moles of cations produced by the dissociation of a mole of electrolyte
ρ_i	Density of a solid phase of species i (kg/m^3)
σ	Conductivity of the electrode (S/m)
σ_{eff}	Effective conductivity of the electrode (S/m)
ϕ_1	Electric potential in the electrode (V)
ϕ_2	Electric potential in the electrolyte (V)
$\Delta\phi_{film}$	Voltage drop across Li$_2$O$_2$ film formation (V)
∇	Differential operator

Subscripts and Superscripts

o	Initial
1	Electrode phase
2	Electrolyte phase
a	Anodic
c	Cathodic
g	Gases
m	Electrode reaction or solid species

the reduction reaction with oxygen according to following reactions:

$$Na^+ + O_2 + e^- \rightarrow NaO_2 \quad (E^0 = 2.27\,V\,vs\,Na^+/Na) \tag{1}$$

$$2Na^+ + O_2 + 2e^- \rightarrow Na_2O_2 \quad (E^0 = 2.33\,V\,vs\,Na^+/Na) \tag{2}$$

$$4Na^+ + O_2 + 4e^- \rightarrow 2Na_2O \quad \left(E^0 = 1.95\,V\,vs\,Na^+/Na\right) \tag{3}$$
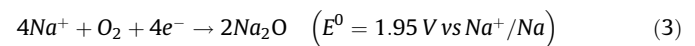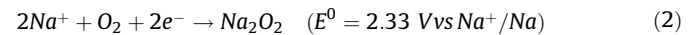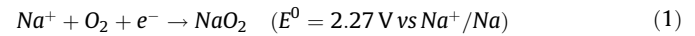
In this respect, Na-air batteries are also regarded as another promising alternative energy storage system and several attempts have been made to build Na-air batteries [13,14]. The feasibility of a liquid-sodium-oxygen cell with polymer electrolytes has been reported and operated at high temperature up to 100 °C to eliminate the sodium dendrite formation at the anode [15]. However, the running of liquid sodium is well known as a highly corrosive characteristic and the high operating temperatures are unsuitable for practical applications. Sun et al. have recently investigated a rechargeable Na-air battery working at room temperature with a carbonate-based electrolyte using dry-air feeding and found that both crystallised sodium peroxide (Na$_2$O$_2$) and amorphous sodium carbonate (Na$_2$CO$_3$) coexist as the discharge products but disappear during the charged process [16]. The thin film electrode based on the weight of carbon film provided an initial discharge capacity of 1884 mAh/g$_{carbon}$ at discharge voltage plateau of 2.3 V. For the initial charge process, this thin film air electrode demonstrated the sluggish diffusion and reaction kinetics of charging processes with the starting charging potential at 3.5 V and ending at 3.9 V [16]. Thus, this system also suffers from similar high overpotential and low energy efficiencies to the Li-air battery when using carbonate-