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Short communication

Ti- and Zr-based metal-air batteries

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HIGHLIGHTS

- A high-temperature Ti or Zr-air battery that shuttles oxygen is proposed.
- A first-principles study predicts a high capacity and voltage for this battery.
- Ti and Zr dissolves oxygen topotactically up to 33% and remains metallic.
- Oxygen is predicted to have a high mobility in TiO_x and ZrO_x at elevated temperature.

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ABSTRACT

We propose a high-temperature, rechargeable metal-air battery that relies on Ti or Zr metal as the anode and the shuttling of oxygen anions between the cathode and the anode through a solid-oxide ion-conducting electrolyte. The cathode has much in common with solid-oxide fuel cells. Key in the proposed battery is the use of Ti or Zr as the anode as these metals are unique in their ability to dissolve oxygen up to concentrations of 33% with minimal structural and volumetric changes. First-principles statistical mechanics calculations predict open circuit voltages around 2.5 V, substantially larger than the open circuit voltage of high-temperature solid-oxide fuel cells. The calculations predict the stability of TiO and ZrO monoxides along with TiO_x and ZrO_x (with x as high as ½) solid solutions. These suboxide phases are all predicted to be metallic, indicating that electron transport in the anodes will not be rate limiting. The oxygen diffusion coefficients in the Ti and Zr suboxides at high temperature (~700–800 °C) are predicted to be comparable to that of Li ions in intercalation compounds. These properties suggest theoretical capacities as high as 840 mAh g^{-1} and 500 mAh g^{-1} for Ti and Zr based metal-air batteries respectively.

1. Introduction

The use of intercalation compounds as electrodes in Li-ion batteries has proven crucial to the success of these electrochemical storage devices, enabling high charge and discharge rate capabilities as well as high cycle lifetimes. Li-intercalation compounds used as electrodes in Li-ion batteries consist of an electronically conducting host structure that can undergo large variations in Li concentration without significant crystallographic modifications [1,2]. A drawback of intercalation compounds, however, is their limited capacity, both by weight and volume. Alternative electrode reaction mechanisms are, therefore, actively investigated [3–10]. One such mechanism, inspired by the Li-air battery [3,6,9], is to dispense of the host structure altogether and to let the shuttled ion react with oxygen in ambient air, thereby forming a metal oxide at the cathode (i.e. Li_2O_2 or Li_2O in the Li-air battery). Although the theoretical capacity of a Li-air battery is substantially higher than can be achieved with intercalation compounds, it nevertheless suffers from sluggish kinetics and large hysteresis between charge and discharge [6,9]. This poor kinetics has its origin in part due to the formation of the electronically insulating and poorly conducting oxide reaction product on the current collector. The Li-air battery has nevertheless sparked interest in other metal-air battery concepts. The challenge there, however, is the difficulty in finding electrolytes that conduct multivalent metal cations.

Here we propose a high-temperature metal-air battery that has much in common with intercalation processes, relying on pure Ti or Zr as the anode. The proposed battery is similar to the high-temperature battery recently developed at CIC EnergiGune [11],

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which shuttles oxygen anions instead of metal cations. Instead of using low melting temperature metals as the anode as in Reference 11, we propose solid Ti or Zr as the anode. We will refer to this type of battery as an oxygen-shuttled metal-air (OSMA) battery. Using first-principles electronic structure calculations, we confirm that Ti and Zr have unusually high oxygen solubilities in the solid state [12–22], remain metallic upon oxygen insertion up to this solubility limit and undergo minor structural and volumetric changes as the concentration of dissolved oxygen is varied. Furthermore, we predict this high-temperature battery to have an open circuit voltage and an oxygen anion mobility (within the anode) that is comparable to that of Li-ion batteries (albeit it at solid-oxide fuel cell operating temperatures).

2. Battery design

A schematic of the proposed battery is illustrated in Fig. 1. The battery consists of (i) a metal anode, (ii) an electrolyte that only allows oxygen ions to pass through but is electronically insulating and (iii) a cathode that is a reservoir containing oxygen gas at a fixed partial pressure. The cathode side of the battery is identical to a high-temperature solid-oxide fuel cell, where a catalyst is needed to dissociate oxygen molecules O_2 into two oxygen anions O^{2-}. A key component of the proposed battery is the use of either Ti or Zr metal as the anode, which are able to dissolve oxygen anions topotactically [20–22] as occurs in Li-ion batteries relying on intercalation compounds. Similar to an intercalation process, oxygen inserts into the hcp crystal structure of the Ti or Zr anode and diffuses to the interior of the metal, thereby raising the overall oxygen concentration of the metal. The anode oxide ion concentration increases during discharge until its oxygen solubility limit is reached, which for Ti and Zr is ~33%.

We first derive a Nernst equation to link the open circuit voltage of this battery to oxygen chemical potentials in the anode and cathode. At open circuit, the battery will reach an equilibrium state at constant temperature and pressure. Hence equilibrium is determined by the minimization of the Gibbs free energy of the battery with respect to internal degrees of freedom. These free to vary degrees of freedom include the concentrations of oxygen in the anode and cathode as well as the concentration of excess electrons within the two electrodes.

$$dG = \mu^{c}_{O_2}\,dN^{c}_{O_2} + \mu^{c}_{e}\,dN^{c}_{e} + \phi^{c}\,dq^{c} + \mu^{a}_{O}\,dN^{a}_{O} + \mu^{a}_{e}\,dN^{a}_{e} + \phi^{a}\,dq^{a}$$

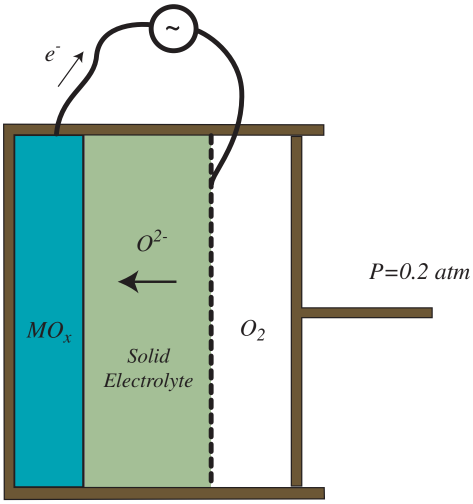

Fig. 1. Schematic of a metal-air battery in which oxygen is shuttled between cathode (air) and a metal anode with a high oxygen solubility (M = Ti or Zr).

In this expression, the superscript "c" ("a") refers to cathode (anode), the "μ"s are chemical potentials and the "ϕ"s are electrostatic potentials within the electrodes. "N" denotes the number of atoms or electrons and "q" denotes the charge. The subscript "O" refers to oxygen, "O_2" to an oxygen molecule and "e" to electron. The electron chemical potential, μ^{a}_{e}, corresponds to the Fermi level in the anode. Only one of the differentials in the above expression for dG is independent due to mass and charge conservation. For convenience, we take $N^{c}_{O_2}$ as the independent variable such that $dN^{a}_{O} = -2\,dN^{c}_{O_2}$, $dN^{c}_{e} = -4\,dN^{c}_{O_2}$, $dq^{c} = -e\,dN^{c}_{e} = 4e\,dN^{c}_{O_2}$, $dN^{a}_{e} = 4\,dN^{c}_{O_2}$ and $dq^{a} = -e\,dN^{a}_{e} = -4e\,dN^{c}_{O_2}$. Substituting these in the differential form of the Gibbs free energy and setting it equal to zero yields:

$$dG = \left(\mu^{c}_{O_2} - 4\mu^{c}_{e} + 4e\phi^{c} - 2\mu^{a}_{O} + 4\mu^{a}_{e} - 4e\phi^{a}\right) dN^{c}_{O_2} = 0$$

or equivalently:

$$\mu^{c}_{O_2} - 4\eta^{c}_{e} - 2\mu^{a}_{O} + 4\eta^{a}_{e} = 0$$

where we have introduced the electron electrochemical potential $\eta_e = \mu_e - e\phi$

The electromotive force when the battery is in open circuit is equal to the difference in electron electrochemical potential across the cathode and anode according to:

$$\text{emf} = -\left(\eta^{c}_{e} - \eta^{a}_{e}\right)/e = -\left(\mu^{c}_{O_2}/2 - \mu^{a}_{O}\right)\Big/2e$$

Hence, the electromotive force is determined by a difference in oxygen chemical potentials across the electrodes of the battery. First-principles statistical mechanical approaches allow us to predict the variation of the oxygen chemical potentials as a function of anode oxide ion concentration and the oxygen partial pressure in the cathode.

3. Methodology

We used a combination of first-principles electronic structure calculations (density functional theory) within the generalized gradient approximation (PBE) as implemented in the Vienna ab initio Simulation Package (VASP, University of Vienna, Austria) [23–26] and statistical mechanics methods to calculate relevant electronic, thermodynamic and kinetic properties of the Ti–O and Zr–O binary systems. This approach has been used extensively in the study of Li-intercalation compounds [27–33]. We accounted for the configurational degrees of freedom associated with the many possible ways of distributing oxygen and vacancies over the interstitial sites of hcp Zr and Ti with the cluster expansion formalism [34,35]. Combined with Monte Carlo simulations, this approach enables the prediction of finite temperature phase stability of ordered and disordered phases, of thermodynamic potentials (free energies and chemical potentials) as well as diffusion coefficients. For the chemical potential of oxygen gas appearing in the above Nernst equation, we used thermodynamic data from the NIST Standard Reference Database [36] with a shift due to [37] to eliminate systematic errors inherent to approximations to density functional theory when going from the gas state (molecular O_2) to the solid state (oxygen dissolved in Zr and Ti).

4. Results

Fig. 2 shows the calculated voltage curves of a ZrO_x and TiO_x based OSMA battery at 300 K and 900 K. The plateaus in the voltage curve are due to two-phase regions and the steps are due to the