Journal of Energy Chemistry 24 (2015) 614–619

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/journal-of-energy-chemistry/

# High-temperature liquid Sn-air energy storage cell

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ARTICLE INFO

*Article history:*
Received 8 July 2015
Revised 10 August 2015
Accepted 10 August 2015
Available online 3 September 2015

*Keywords:*
Nano tin
Metal-air battery
Solid oxide electrolyte
Thermal oxidation
Discharge behavior

ABSTRACT

A new type of a high temperature liquid metal-air energy storage cell based on solid oxide electrolyte has been successfully demonstrated at 750 °C by feeding metal Sn. In order to understanding the initial size effect of metal as a liquid fuel, we report here the impact of the thermal and electrochemical oxidation behavior of nano Sn (~100 nm), comparing with micro-sized (~5 μm) and macro-sized (~350 μm) Sn. The thermogravimetric analysis and the monitoring OCV test indicate that the distinct property of nano-sized Sn results in a favorable thermal oxidation behavior near the melting point and a promising power performance due to enhanced fuel transport to the anode. However, the accumulated Sn oxide at the reaction interface during a discharge test towards the limitation of further electrochemical oxidation.



## 1. Introduction

Metal-air batteries have been intensively explored as an alternative future energy storage and conversion systems owing to their intrinsically high energy and power densities, the relatively mature research on air electrode, and cost effective composition of non-noble fuel electrode, as well as in response to the high energy demand for portable devices and electric vehicles even stationary power plants [1–5]. Of late, research into the metal-air techniques has been focused on Zn-air (~1000 Wh/kg), Li-air (~13,000 Wh/kg), and Ge-air (~1500 Wh/kg) batteries because of its very high specific energy and energy density with open cell air cathode structure [3–6]. With these devices, however, the electrochemical energy could be stored in the stationary part as a form of sacrificial metal anode. This distinct architecture would make a limitation approach for large-scale commercialization unless the anode can provide good electrochemical reversibility and high cyclic durability.

As a feasible alternative to continuous operation, recently, a high temperature liquid metal-air energy storage cell (LMAESC) in conjunction with a solid oxide electrolyte has been investigated applying post-transition metals such as In [7], Sn [7–17], Sb [18–25], Pb [7], and Bi [12] as a sacrificial electrode, so-called liquid metal anode (LMA). Since these liquid metals has relatively low melting point, it can improve the anode polarization by incorporating liquid wetting materials to spread on the solid ceramic surfaces such as yttria-stabilized zirconia (YSZ) electrolyte and Ni-YSZ anode. Another approach is to operate in a direct carbon fuel cell in order to enhance wetting of solid carbon fuels at anode/electrolyte interface as an electrochemical mediator [26–31].

This concept first employed, in 1989 by Costa et al. [32], using a fused Fe gasifier reactor in order to utilize solid coal. Gopalan et al. [33,34] reported liquid metal Ag and Sn, as a consumable feed dispersed in a Ni-YSZ anode and the system suggested in two different modes: (i) in a solid oxide electrolyzer mode to generate hydrogen gas using coal and steam and (ii) in a solid oxide fuel cell (SOFC) mode to produce electricity using hydrogen. CellTech Power [8–11] has energetically developed a liquid tin anode solid oxide fuel cell (LTA-SOFC) over more than a decade to operate various carbonaceous fuels. The role of LTA is a non-structural fluid cell component so it is highly tolerant of impurities. Gorte and his group [7,12,13,18–20,25] also proposed that various liquid metal (In, Pb, Sb, Sn, Bi, and Ag) fuel cells and flow batteries based on the SOFC. Specially, they focused on molten $Sb/Sb_2O_3$ anode and the direct utilization of sugar char and bio-oil was examined that the stable operation with a peak current density of around 250 mW/cm$^2$ at a constant voltage of 0.5 V was demonstrated for up to 250 h [20]. Similarly, Shi et al. [14,21–24] has reported using liquid metallic Sb and Sn in terms of the effect of the interface morphology of the electrolyte, the influence of temperature in the metal/metal oxide interaction, and the reaction kinetics. Currently, the LMA SOFC was studied on the transport behavior of oxygen in the bulk surface Sn and the thermochemical partitioning of coal contaminates in the LMA system by National Energy Technology

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http://dx.doi.org/10.1016/j.jechem.2015.08.006
2095-4956/

**Table 1.** Summary of theoretical properties, electrochemical reaction for possible high temperature liquid metal-air energy storage cell. Theoretical open circuit voltage for the electrochemical oxidation calculated based on thermodynamic data [39,50–52]. Theoretical capacity calculated based on active fuel metals only, including $O_2$ but not air.

| | m.p. (°C) | Electrochemical oxidation reaction | OCV (V) at 750 °C | Energy density (kWh/L) at 750 °C |
|---|---|---|---|---|
| $^{49}$In | 157 | $2In + 3O^{2-} \rightarrow In_2O_3 + 6e^-$ | 0.98 | 4.84 |
| $^{50}$Sn | 232 | $Sn + 2O^{2-} \rightarrow SnO_2 + 4e^-$ | 0.96 | 6.25 |
| $^{51}$Sb | 630 | $2Sb + 3O^{2-} \rightarrow Sb_2O_3 + 6e^-$ | 0.75 | 3.31 |
| $^{82}$Pb | 327 | $Pb + O^{2-} \rightarrow PbO + 2e^-$ | 0.65 | 2.20 |
| $^{83}$Bi | 272 | $2Bi + 3O^{2-} \rightarrow Bi_2O_3 + 6e^-$ | 0.48 | 1.64 |

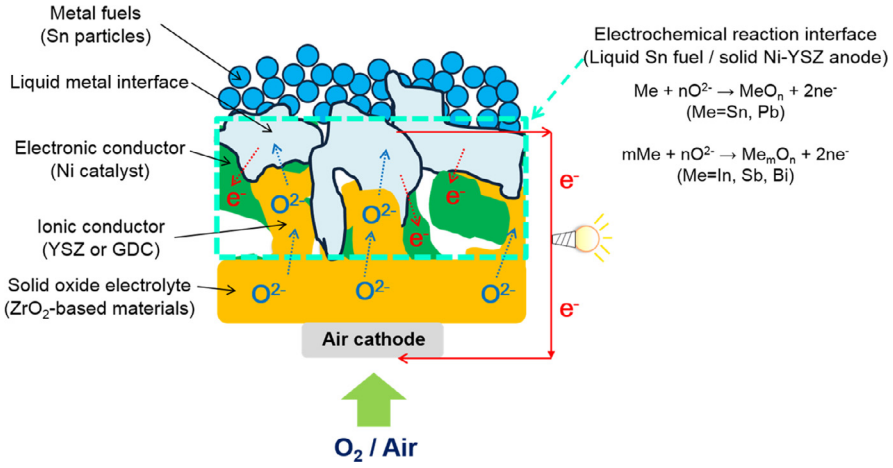


**Fig. 1.** A schematic of a high-temperature liquid metal-air energy storage cell using solid oxide electrolyte membrane.

Laboratory (NETL) [35,36]. Otaegui et al. [37] tested a high temperature liquid metal-air battery at a current density of 10 mA/cm$^2$ at 800 °C. The discharge capacity was achieved around 4–13 mAh/cm$^2$ with more than 1000 charge/discharge cycles by applying the electrochemical treatment of the cell.

Among liquid metal candidates facing the development of the LMAESC, Sn is very attractive material due to its relatively low melting point (232 °C), high volumetric energy density (6.25 kW/h), and low cost (US$ 22.27 kg$^{-1}$) [38], as summarized in Table 1. The liquid Sn metal can be galvanically oxidized to $SnO_2$ owing to the negative Gibbs free energy change of −365 kcal/mol at 750 °C [39].

$$Sn + 2O^{2-} \rightarrow SnO_2 + 4e^- \; E^0 = 0.96\,V \quad (1)$$

Fig. 1 represents a schematic of the operation principle of a LMAESC cell via high-temperature solid oxide electrolytic route. Despite these attractive benefits, the use of liquid metal fuels is still challenging because of the formation of insulating oxide layers at reaction site, high surface tension and sluggish oxygen-ion migration through the solid electrode interface [7,14,35–37]. Moreover, most of these studies applied the bulk sized metal sources and there is no distinct report on the effect of different size of metal particles on the energy storage and conversion performance.

Here we have studied new insight regarding the energy storage performance of the LMAESC based on solid oxide electrolytes and the effect of the initial metal fuel size on the thermal- and electro-oxidation behaviors using a thermogravimetric analysis (TGA) and an in-house built high temperature fuel cell test station.

## 2. Experimental

Three different sizes of Sn particles were purchased from Sigma-Aldrich: macro-sized (> 250 μm, average size 350 μm, purity > 99%), micro-sized (< 45 μm, average size 5 μm, purity > 99.8%), and nano-sized (< 150 nm, average size 100 nm, purity > 99%) Sn, as shown in Fig. 2. Before an energy storage performance test, thermogravimetric analysis (TGA; Shimadzu TGA-50A, Japan) was carried out to find out the relationship between thermal oxidation behaviors and electro-catalytic oxidation characteristics of Sn particles.

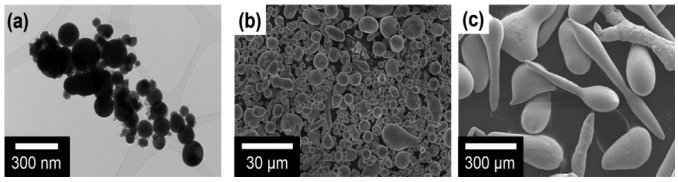


**Fig. 2.** Images of as-received Sn particles: TEM image of (a) nano-sized Sn, SEM images of (b) micro-, and (c) macro-sized Sn.

The electrolyte-supported button-shaped SOFC single cell (NEXT-CELL, Fullcellmaterials, USA) consisted of a porous Ni-GDC/Ni-YSZ anode (50 μm), a dense $ZrO_2$-based electrolyte (150 μm) and a porous LSM/LSM-GDC cathode (50 μm), as detailed in Fig. 3. The diameter of the cell was 28 mm and the active area corresponding to the cathode layer was 1 cm$^2$. Pt wires (99.99%, 0.5 mm, Alfa Aesar) and Pt mesh (99.9%, 52 mesh woven, Alfa Aesar) were applied as a current collector. In order to prevent air leakage, two gaskets (Thermiculite 866, USA) in the form of rings were mounted with a sandwich arrangment of the cell and then ceramic adhesive (Aremco 668, USA) was pasted around the alumina tubes. Sn fuels were prepared with 1 g of Sn powders and dissolved in 0.2 mL of ethylene glycol (Junsei Chemical Co., Ltd., Japan). The Sn-air energy storage cell was performed by placing the as-prepared Sn fuel slurry directly into the anode.

Prior to heating up the system, inert Ar gas (purity 99.999%, 50 mL/min) was flowed through the anode chamber to remove residual gas for over 1 h. The oxygen sensing measurement (NeoFox, Ocean Optics, USA) was conducted the reactor outlet. In the experiment,