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Performance and stability of a liquid anode high-temperature metal–air battery

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HIGHLIGHTS

- A new energy storage device is presented.
- High energy densities are predicted from theoretical estimations.
- Degradation processes are reversible and concept is fully rechargeable.
- Long term stability of the Sn–air battery is demonstrated.

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ABSTRACT

A High-Temperature Metal–Air Battery (HTMAB) that operates based on a simple redox reaction between molten metal and atmospheric oxygen at 600–1000 °C is presented. This innovative HTMAB concept combines the technology of conventional metal–air batteries with that of solid oxide fuel cells to provide a high energy density system for many applications. Electrochemical reversibility is demonstrated with 95% coulomb efficiency. Cell sealing has been identified as a key issue in order to determine the end-of-charge voltage, enhance coulomb efficiency and ensure long term stability. In this work, molten Sn is selected as anode material. Low utilization of the stored material due to precipitation of the SnO_2 on the electrochemically active area limits the expected capacity, which should theoretically approach 903 mAh g^{-1}. Nevertheless, more than 1000 charge/discharge cycles are performed during more than 1000 h at 800 °C, showing highly promising results of stability, reversibility and cyclability.

1. Introduction

Rechargeable or secondary batteries have been widely used for electronics, stationary and automotive applications. They have been identified as one of the most important enabling technologies in the 21st century due to their significant roles in a green and sustainable energy future. There are many types of rechargeable batteries such as lead-acid, nickel-cadmium, nickel-metal hydride, vanadium redox flow, sodium-sulphur and lithium-ion batteries. Among them, Li-based battery is one of the most advanced and has found widespread applications in the past twenty years. However, current batteries are not keeping up with the demand in terms of energy, power, safety, life and cost. Future batteries will need new chemistries, innovative material concepts, and revolutionary cell designs and manufacturing techniques.

One of the potential systems is metal–air battery such as Li–air or Zn–air. A lithium–air battery typically includes a lithium–metal negative electrode, a positive electrode where reaction with oxygen occurs, e.g. from air, sometimes referred to as an "oxygen positive electrode", and an electrolyte or other ion conducting medium in fluid communication with both the positive and the negative electrodes. Typically, in non-aqueous systems, lithium and oxygen react to produce lithium peroxide.

On the other hand, solid oxide fuel cells (SOFCs) have been developed as a promising technology that converts the chemical

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energy from a fuel directly into electricity through an electrochemical reaction with oxygen [1]. The major feature of a SOFC is its solid electrolyte which is an oxygen ion conductor. It also has a cathode and an anode where half-cell reactions take place. At the cathode, oxygen is reduced into oxygen ions that are then transported to the anode through the solid electrolyte. At the anode, oxygen ions react with hydrogen-containing fuels to form water, releasing electrons to an external circuit.

Particularly, there is a SOFC that contains a liquid tin layer as part of the anode which can be used for direct power generation from coal or JP8 fuel [2–6]. In such a system, liquid tin fully covers the active oxygen ion exchange area between the electrolyte and the anode and participates as an intermediary for the oxidation of fuel delivered to the fuel cell. In addition, it serves as a buffer against fuel contaminants, as it blocks the transport of insoluble or slag-forming constituents to the electrolyte and impedes the transport of soluble fuel contaminants, thereby reducing the rate of reactions between contaminants and the electrolyte. It is also postulated that the usage efficiency of electrolyte surface is improved over existing porous solid anode technology because the liquid layer fully covers the electrolyte. Hence, oxygen ion reactions can be expected to occur over the full surface of the electrolyte when using a liquid anode, instead of only around triple phase boundaries between the fuel, anode and electrolyte. Jayakumar et al. [7] reported such a device in which Sn and Bi were examined at 973 and 1073 K as anodes in SOFCs with yttria-stabilized zirconia (YSZ) as electrolyte. Although open circuit voltages (OCV) were close to that expected based on their oxidation thermodynamics, their intention was to use molten metal as a medium to transfer oxygen to solid fuels such as coal. Therefore, these systems were still used as energy conversion devices.

Tao et al. [8,9] describe rechargeable devices which have a dual-mode capability. Those devices can operate as a fuel cell and as a battery, and include a liquid metal anode, an electrolyte and a cathode. However, they need to be recharged with a chemical source in order to operate in dual form and only act as a battery for a short period of time when the fuel supply (chemical source) is exhausted or interrupted. Therefore, these systems cannot be considered as pure electric energy storage devices since a chemical reductant is required to reduce the oxidized anode.

Here we propose a metal–air battery [10] in which oxygen ions diffuse through a solid oxide electrolyte between electrodes, where the metal anode works in a melt or semi-melt state, allows the electrochemical reactions to take place and overcomes the problems derived from the use of conventional metal–air batteries. This metal–air battery concept combines the technology of conventional metal–air batteries and SOFCs to provide a high energy storage system for many utility applications. It operates at high temperature, typically between 600 and 1000 °C and uses the cathode and the electrolyte of SOFCs, but metallic fuel is stored as in metal–air batteries. The electrochemical reactions that take place in the new battery system are completely different from those in metal–air batteries or SOFCs as shown in Fig. 1. Contrary to other electrochemical devices that combine the technology of metal–air batteries and solid oxide fuel cells, the HTMAB is only electrically rechargeable and operates as a pure electric energy storage device.

This technology provides a battery system with higher energy density than lithium-ion batteries due to the high specific capacity of metal anodes (i.e. 903 mAh g^{-1} for Sn). Moreover, solid oxide electrolytes prevent short-circuit from happening and are more stable than conventional liquid electrolytes used in Li-ion and Li–air batteries. Volatilization and flammability problems are also

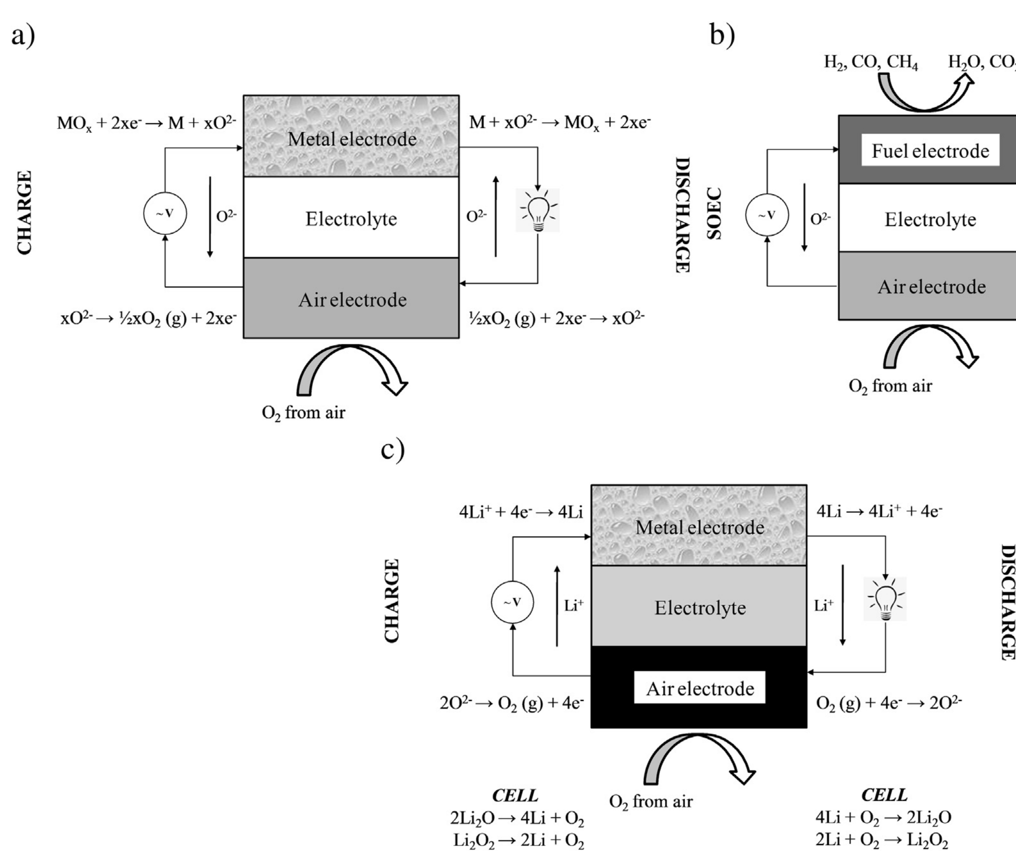

Fig. 1. (a) Electrochemical reactions in HTMABs, (b) SOFCs and (c) lithium–air batteries.