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Technical feasibility of a proton battery with an activated carbon electrode

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ABSTRACT

The technical feasibility of a small-scale 'proton battery' with a carbon-based electrode is demonstrated for the first time. The proton battery is one among many potential contributors towards meeting the gargantuan demand for electrical energy storage that will arise with the global shift to zero greenhouse emission, but inherently variable, renewable energy sources. Essentially a proton battery is a reversible PEM fuel cell with an integrated solid-state electrode for storing hydrogen in atomic form, rather than as molecular gaseous hydrogen in an external cylinder. It is thus a hybrid between a hydrogen-fuel-cell and battery-based system, combining advantages of both system types. In principle a proton battery can have a roundtrip energy efficiency comparable to a lithium ion battery. The experimental results reported here show that a small proton battery (active area 5.5 cm²) with a porous activated carbon electrode made from phenolic resin and 10 wt% PTFE binder was able to store in electrolysis (charge) mode very nearly 1 wt% hydrogen, and release on discharge 0.8 wt% in fuel cell (electricity supply) mode. A significant design innovation is the use of a small volume of liquid acid within the porous electrode to conduct protons (as hydronium) to and from the nafion membrane of the reversible cell. Hydrogen gas evolution during charging of the activated carbon electrode was found to be very low until a voltage of around 1.8 V was reached. Future work is being directed towards increasing current densities during charging and discharging, multiple cycle testing, and gaining an improved understanding of the reactions between hydronium and carbon surfaces.

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Introduction

Electrical energy storage technologies are now widely accepted as a critical enabling technology in the transition to a global sustainable energy economy [1-4]. Such an energy economy needs to supply affordable energy services to the entire world population while protecting the earth's climate

and guaranteeing energy security. In particular, electrical energy storage is required to ensure continuous and reliable supply from zero greenhouse emission, but essentially variable, renewable energy sources such as solar wind and wave power. It is also an integral part of zero-emission transport systems using electric drives, whether hybrid petrol-electric, battery electric, or hydrogen fuel cell vehicles for road, rail or sea [3].

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As the world moves towards renewable energy to reduce greenhouse emissions and limit the mean global temperature increase to 1.5 °C above preindustrial levels [5], requirements for electrical energy storage will be very large indeed. Counting storages for large electricity grids (bulk and distributed), microgrids and standalone applications, as well as electricdrive transport vehicles, the total required is likely be well above 10% of total global electricity consumption [6], that is, over 2000 TWh with 2014 as the basis [3].

While most likely a range of energy storage technologies will be deployed, the associated material resource demands will be enormous. An indication of the scale of this impact is the doubling in world lithium demand (2016 level) that would arise if output from the Tesla 'Gigafactory' for Li ion batteries meets its 2018 target [7].

In meeting this gargantuan future demand for electrical energy storage, fundamental considerations are:

- high roundtrip energy efficiency to minimise system size and mass for a given amount of effective storage,
- availability of the raw materials in sufficient bulk quantities,
- the cost of these materials, and
- the mass and volume of the storage systems per kWh stored, that is, their gravimetric and volumetric energy densities.

These considerations have guided the development of a 'proton battery' with a carbon-based electrode as reported in the present paper, as one among many technological options that merits investigation over the revolutionary period in the energy sector that is already upon us.

A proton battery is a hybrid between a hydrogen-fuel-cell and battery-based system, seeking to combine the unique advantages of both types of system. The concept was first proposed in 2014 by Andrews and Seif Mohammadi [8] working at RMIT and is shown in Fig. 1. The arrangement was originally termed a 'proton flow battery', because in charging mode an inflow of water is needed to provide the source of protons. We have subsequently shortened the name to simply a 'proton battery'. Both high gravimetric and volumetric energy densities of a hydrogen-based electricity supply system are especially important for on-vehicle applications, to provide a range competitive with petrol or diesel vehicles without a prohibitive weight and space penalty. While often not being so critical, a high gravimetric energy density is usually still advantageous for stationary applications as well, since heavier systems require more expensive support structures, and are more costly to carry to a site or move from site to site (particularly if remote). The volumetric constraints for a stationary system will be site dependent but generally it is beneficial to minimise the volume of the unit for a given level of electricity storage and power output.

The relationship of this concept to, and its essential differences from, related earlier designs by the Fiat Research Centre [9], Condon and Schober [10], Ovshinsky et al. [11], and very general patents taken out by General Electric Company [12–14], were described in Andrews and Seif Modhammadi [8]. The first proton battery (Fig. 1) was basically a PEM Unitised Regenerative Fuel Cell (URFC) [15-17] with an integrated solidstate electrode for storing hydrogen in atomic (H), rather than molecular gaseous (H₂) form. Protons produced during electrolysis (actually as hydronium, H₃O⁺ ions) are conducted through the nafion membrane and enter the solid-state storage to form a bond with the storage material, without combining in pairs with electrons to form hydrogen gas. In fuel cell mode this process is reversed, with hydrogen atoms being released from the storage and giving up an electron to become protons once again. These protons then re-enter the membrane (as H_3O^+) and move back to the oxygen side where they combine with oxygen and electrons from the external circuit to re-form water. It is this water-formation reaction that drives the whole process in discharge mode, as it does on the oxygen/air electrode (cathode) of a conventional PEM fuel cell.

Therefore, in the proton battery, many processes in the conventional hydrogen-based energy storage system that cause energy losses and irreversible entropy increases are omitted, such as hydrogen gas evolution and compression, and the splitting of molecular hydrogen into protons in fuel



Fig. 1 – The novel proton battery system employing a reversible fuel cell with integrated solid proton storage electrode, as proposed in 2014 by Andrews and Seif Mohammadi [8]. M represents an atom of the solid storage medium to which a hydrogen atom is bonded.

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