



Platinum-rare earth cathodes for direct borohydride-peroxide fuel cells



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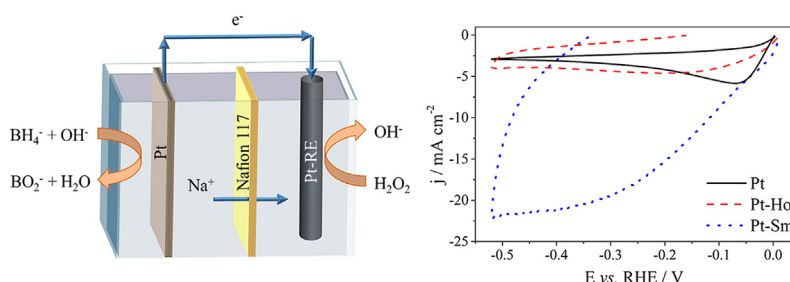
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HIGHLIGHTS

- Platinum-rare earth (RE = Sm, Dy, Ho) alloys were prepared by arc melting.
- SEM/EDXS and XRPD corroborate alloys morphology, composition and structure.
- Hydrogen peroxide reduction reaction with 1.9 electrons exchanged at Pt–Sm electrode.
- Borohydride fuel cell with Pt–Sm cathode doubles the power density of that using Pt.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrogen peroxide (H_2O_2) is being actively investigated as an oxidant for direct borohydride fuel cells. Herein, platinum-rare earth (RE = Sm, Dy, Ho) alloys are prepared by arc melting and their activity for hydrogen peroxide reduction reaction (HPRR) is studied in alkaline media. Cyclic voltammetry and chronoamperometry measurements show that Pt–Sm electrode displays the highest catalytic activity for HPRR with the lowest activation energy, followed by Pt–Ho, while Pt–Dy alloys show practically no activity. Laboratory direct borohydride-peroxide fuel cells (DBPFCs) are assembled using these alloys. The DBPFC with Pt–Sm cathode gives the highest peak power density of 85 mW cm^{-2} , which is more than double of that obtained in a DBPFC with Pt electrodes.

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1. Introduction

Fuel cells are silent and ecological electrochemical devices that convert chemical energy directly into electrical energy with an efficiency of 50–70%, having several advantages compared to energy production from combustion of fossil fuels [1]. Among the several types of fuel cells developed, those operating at low

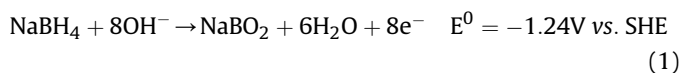
temperatures ($<80 \text{ }^\circ\text{C}$), such as polymer electrolyte fuel cells (PEFCs), are considered promising power sources for portable applications [2].

Pure hydrogen (H_2) generated from water electrolysis can act as a fuel in PEFCs. However, due to its high production cost, safety and storage issues, H_2 can be replaced by alternative liquid feeds, such as methanol, ethanol, propanol and ethylene glycol [3–5]. Although fuel cells fed with methanol, known as direct methanol fuel cells (DMFCs), are attractive because of system simplicity and low cost, they have some limitations due to low electrochemical activity, methanol crossover and low open circuit potential [6,7].

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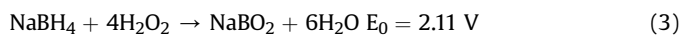
One way of overcoming these problems is by using alternative hydrogen carrying sources, such as borohydride compounds as fuel in direct borohydride fuel cells (DBFCs). Sodium borohydride (NaBH_4) has a specific capacity of 5.67 A h g^{-1} and a hydrogen content of 10.6 wt.% [1]. Moreover, NaBH_4 can be oxidised in alkaline medium, giving rise to a maximum of eight electrons for molecular unit, according to Eq. (1). The inert and non-toxic NaBO_2 formed in the reaction can be recycled back to NaBH_4 [8].



Normally, oxygen (O_2) is used as the oxidant in fuel cells [1], but recently hydrogen peroxide (H_2O_2) has been pointed out as a substitute for O_2 in the cathodic compartment, where the two-electron hydrogen peroxide reduction reaction (HPRR) can be described by Eq. (2).



Two-electron H_2O_2 reduction has lower activation barrier compared to the four-electron O_2 reduction and, consequently, has faster kinetics. Furthermore, the standard electrode potential, E^0 , for direct H_2O_2 reduction is higher than that for O_2 reduction, so DBFC using H_2O_2 as an oxidant has higher cell voltage (Eq. (3)).



Thus, DBFCs operating with H_2O_2 , known as direct borohydride-peroxide fuel cells (DBPFCs) have several advantages when compared to conventional H_2/O_2 fuel cells, namely lower activation energy, high energy density, easy handling, longer cycle life and environmental safety [9,10]. However, in the presence of some materials, such as transition metal salts, the chemical decomposition of H_2O_2 (into O_2 and H_2O) at higher temperatures is the main limitation of this oxidant [11].

One of the most critical points of fuel cell optimisation is the selection of the electrode materials. In DBPFCs the most commonly used electrodes for the anodic reaction contain platinum (Pt), gold (Au), and palladium (Pd) [12–15]. These catalysts were identified to have good performance for the cathodic reaction in these devices as well [16,17]. Considering the high price of noble metals, cheaper materials have also been evaluated for HPRR. Taking into account their low cost, perovskite-type materials have been reported to have somewhat reasonable activity for HPRR [18,19], although well below that of typical noble-metal electrocatalysts. Therefore, alloys and composites of noble metals with cheap materials are now receiving a great deal of attention [20–23].

Rare Earths (REs) present the largest group of elements with similar chemical, but notably different physical properties as a consequence of their electronic structure. Despite being called “Rare Earths”, elements of this group are as abundant as other elements that are used on daily bases, such as Cu or Pb. Tm is the least abundant of all REs, but it is still notably more abundant than Pt. Thus RE price is significantly lower than price of Pt, reflecting on the fuel cell price and their large-scale production. However, mentioned chemical similarity poses difficulties in REs separation and isolation of the individual elements from the minerals. Thus, though first REs have been discovered two centuries ago, study of these elements and their exploitation is still at the early stage [24].

REs have incomplete, partially filled 4f levels, with only few exceptions (Y, La, Yb, and Lu). Unfilled 4f levels lead to a variety of optical and magnetic properties of RE elements and their compounds. They are known to form a range of intermetallic compounds with transition elements, such as Fe, Co and Ni, which

enable their application in electrochemical energy conversion devices. These intermetallic compounds have been reported to store H_2 in the form of hydrides, with Ni-RE-hydride batteries being new generation energy sources [25].

Furthermore, platinum-rare earth (Pt-RE) alloys have been recently reported to possess good electrocatalytic activity for borohydride oxidation reaction (BOR), hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) [13,24,26–28]. Jakšić considerations on the Brewer-Engel valence bond theory [29] suggested Pt-RE interfaces as systems of interest for application in DBFCs and other PEFCs, depending on the content and nature of the alloy. Namely, alloying of Pt as hyper-d-electronic element with RE as hydride forming hypo-d-electronic element results in the formation of d-transition metal composite with enhanced electrocatalytic activity. This synergistic effect between the components has shown to contribute significantly to an increase of the electrocatalytic activity, with the alloys showing improved performance relatively to the individual parent metals. For instance, platinum-dysprosium (Pt-Dy) alloys tested for BOR exhibited higher number of electrons transferred than Pt [24]. Among other Pt-RE alloys studied for BOR, platinum-holmium (Pt-Ho) showed the highest activity, followed by platinum-samarium (Pt-Sm), while platinum-cerium (Pt-Ce) showed the lowest activity [13]. When these Pt-RE alloys were studied for HER, they all proved to be suitable electrode materials with higher activity compared to pure Pt [26,27].

The present study aims to investigate the electrocatalytic activity of Pt-RE electrodes, with the RE being Sm, Dy, or Ho, for HPRR in alkaline media through cyclic voltammetry and chronoamperometry measurements. To the authors knowledge this is the first time that the use of Pt-RE alloys for HPRR is reported. Then, the efficiency of a DBPFC using the studied electrodes was assessed by assembling a laboratory $\text{NaBH}_4/\text{H}_2\text{O}_2$ fuel cell and estimating the corresponding cell parameters.

2. Experimental

2.1. Preparation and characterisation of the electrodes

Three of the tested Pt-RE (RE = Sm, Dy, Ho) alloys had equiatomic compositions ($\text{Pt}_{0.5}\text{Sm}_{0.5}$, $\text{Pt}_{0.5}\text{Dy}_{0.5}$ and $\text{Pt}_{0.5}\text{Ho}_{0.5}$) with an additional electrode with 40 at% Pt ($\text{Pt}_{0.4}\text{Dy}_{0.6}$) also being tested. The alloys were prepared as described elsewhere [13,27,30] using arc melting in an inert atmosphere starting from stoichiometric amounts of the corresponding elements (Pt, 99.99 wt.%, Johnson Matthey & Co. Ltd., London, UK and Sm, Dy, Ho, 99.9 wt.%, Koch Chemical Ltd., Hertford, UK). The samples were re-melted several times to ensure their homogeneity. A commercial Pt electrode (Metrohm 6.0305.100) was also used for comparison purposes.

Alloys were characterised by optical microscopy (Leica MC 170 HD) and scanning electron microscopy (SEM, EVO 40, Carl Zeiss SMT Ltd., Cambridge, England) coupled with electron probe microanalysis based on energy dispersive X-ray spectroscopy (EDXS) for microstructure examination and qualitative/quantitative phase analysis. The software package Inca Energy (Oxford Instruments, Analytical Ltd., Bucks, UK) was used to process X-ray spectra. Samples were prepared for SEM/EDXS analysis by embedding in a phenolic hot mounting resin with carbon filler, which was then grounded by SiC abrasive papers and polished in steps by using diamond pastes with particle size decreasing from 6 to 1 μm , in order to obtain smooth surfaces. X-ray diffraction on powder samples was performed by means of a diffractometer Philips X'Pert MPD (Cu-K α radiation, step mode of scanning) in order to confirm the crystal structures of the detected phases.

The electrodes were prepared by gluing each alloy button to a

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