

## CONTENT

- 1) Experimental Section
- 2) Stability Measurements
- 3) References

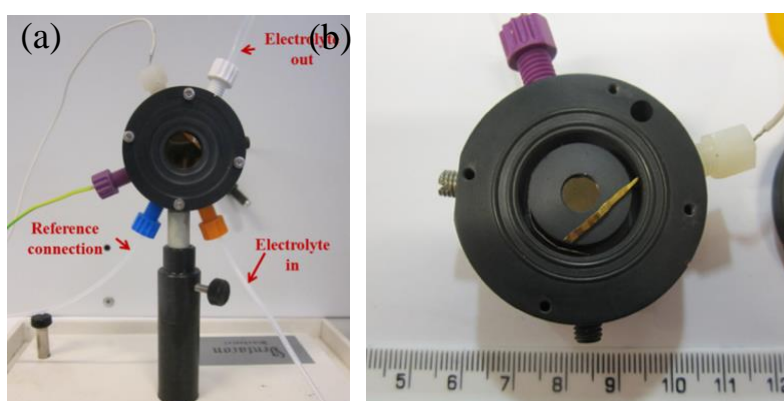
### 1) Experimental Section

The  $\text{LaNi}_{4.7}\text{Sn}_{0.2}\text{Cu}_{0.1}$  base alloy was prepared from high-purity metals by the arc melting technique under an inert gas atmosphere.<sup>[1]</sup> After that, the sample was ground. The Pt modified catalyst,  $\text{LaNi}_{4.7}\text{Sn}_{0.2}\text{Cu}_{0.1} - \text{Pt}$ , was prepared by galvanic displacement. This process involved the immersion of the metal hydride alloy in a  $1.0 \text{ mol L}^{-1}$  of KOH solution containing  $10^{-2} \text{ mol L}^{-1}$  of borohydride for two hours. After that, the material was immersed in KOH  $0.5 \text{ mol L}^{-1}$  solution containing  $10^{-2} \text{ mol L}^{-1}$  of Pt ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) for more two hours.

To prepare the working electrode initially a mixture of 70 mg of catalyst, 30 mg of carbon, 0.984 mL of water, 0.200 mL of iso-propanol and 0.516 mL of Nafion (5 – 10 % of water) was formed. This mixture was sonicated for 30 min and homogenized for 2 min and after that approximately 10 mg of this ink was painted on the carbon paper. To improve the conductivity and the blend, the electrodes were hot pressed for 5 min at  $180 \text{ }^\circ\text{C}$ .

The *in situ* XRD measurements were performed on beamline I11 at the Diamond Light Source, UK. The beamline is an in-vacuum undulator insertion device located on the main electron storage ring.<sup>[2]</sup> The 2 m device has an array of 90 permanent magnets ( $\text{Sm}_2\text{Co}_{17}$ ) with a period length of 22 mm designed to produce x-rays ranging from 5 to 30 keV. The beams produced by these devices in a third generation synchrotron such as Diamond have a low divergence of  $\sim 25 \text{ } \mu\text{rad}$  (vertically) and  $\sim 100 \text{ } \mu\text{rad}$  (horizontally), which should result in a small final beam size at the sample position (2.5 mm x 1.5 mm).<sup>[2]</sup> During the scan the detectors are gated at sufficient frequency to give a nominal  $2\theta$  interval of  $0.0008^\circ$  and  $2\theta$  values recorded from the  $2\theta$ -circle encoders.

*In situ* XRD was considered here to investigate the phase transitions of the alloys when the electrodes were charged/discharged. Fig. S1 shows photographs of the flow cell used for the *in situ* XRD measurements.<sup>[2]</sup> The orange connection, in the Fig. S1a, is the electrolyte inlet of the cell, while the white connection is the outlet. The purple connection is the counter electrode and the blue is the reference electrode. The gold wire, in Fig. S1b, is the contact for the working electrode. The flow rate of the electrolyte used was enough to avoid formation of bubbles during the measurements, which interfere with the obtained results.



**Figure S1.** Photographs of the cell used for the *in situ* XRD experiments.

Data were collected *in situ*, in an electrochemical cell, without and with sodium borohydride  $10^{-2}$  mol L<sup>-1</sup> in a mild alkaline solution (KOH 1.0 mol L<sup>-1</sup>). XRD patterns were collected during the electrochemical charge and discharge processes and also during the exposure to borohydride followed by electrochemical discharge. Data were also collected for dry electrodes.

## 2) Stability Measurements

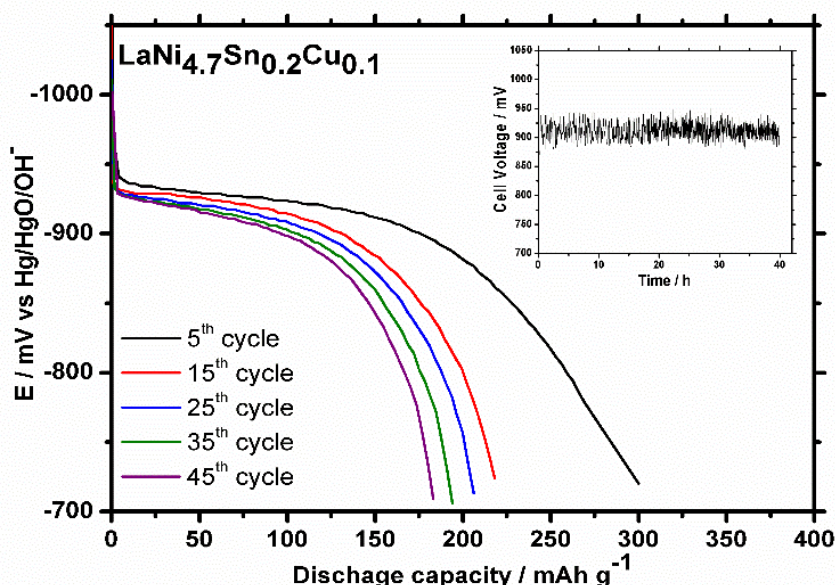


Figure S2: Electrode potential as a function of the discharge capacity for LaNi<sub>4.7</sub>Sn<sub>0.2</sub>Cu<sub>0.1</sub> alloy during the discharge step (at 200 mA g<sup>-1</sup>), along charge/discharge electrochemical multicyclings. Numbers represent the charge/discharge numbers. Inset: Single Cell potential versus time for continuous LaNi<sub>4.7</sub>Sn<sub>0.2</sub>Cu<sub>0.1</sub> anode operation at 200 mA g<sup>-1</sup> in the presence of borohydride ions (1.0 mol L<sup>-1</sup>) in a DBFC (6.0 mol L<sup>-1</sup> KOH electrolyte) working with O<sub>2</sub> fed Pt/C cathode (1 atm).

Experiments reported in Fig. S2 were conducted, similarly to those described for Figure 1, using 6.0 mol L<sup>-1</sup> KOH electrolyte. For the inset, a DBFC fuel unit cell was assembled presenting a configuration closed to that a proton exchange membrane fuel cell (see reference [4] for details) with 5 cm<sup>2</sup> geometric active area. The membrane and electrode assembly was prepared using Nafion 212 (DuPont) membrane and a mixture of carbon powder (Vulcan XC 72) with the LaNi<sub>4.7</sub>Sn<sub>0.2</sub>Cu<sub>0.1</sub> particles in the anode (30.0 mg alloy cm<sup>-2</sup>) and a commercial Pt/C (Etek, 20 wt.% Pt/C) catalyst in the cathode (0.4 mg Pt cm<sup>-2</sup>). KOH electrolyte (6.0 mol L<sup>-1</sup>) with 1.0 mol L<sup>-1</sup> sodium borohydride was continuously fed to the anode, while a O<sub>2</sub> flow at atmospheric pressure was supplied to the cathode. In the inset of Fig. S2, the cell potential is plotted as function of time for a constant current DBFC operation of 6.0 mA cm<sup>-2</sup>, or equivalently 200 mA g<sup>-1</sup> of the alloy contained in the anode at 60 °C.

Results in Fig. S2 evidence a decrease of the metal hydride electrode potential and of the maximum discharge capacity along the multicycling, and this is explained in terms of a continuous alloy degradation due to the pulverization and subsequent oxidation of the particle surface during the repeated charge–discharge cycles, as observed for many other metal hydride alloy systems [5]. As seen in this paper, this alloy cracking is related to the expressive and repetitive alloy unit cell expansion/contraction occurring along the multicycling.

The result in the inset in Fig. S2 denotes a quite stable voltage response of the DBFC, and this implies that either the cathode and anode must maintain stable their respective potentials. In this case, the anode works with the same discharge rate (200 mA g<sup>-1</sup>), as those in the electrochemical multicycling, but in the presence of borohydride. As shown before, under this operating conditions, the anodic reaction involves the continuous hydriding of the LaNi<sub>4.7</sub>Sn<sub>0.2</sub>Cu<sub>0.1</sub> alloy followed by oxidation of the inserted hydrogen atoms. [1] In our work, it is seen that this insertion is small, only

leading the formation of the alpha phase, resulting in much smaller localized stress in the alloy, compared that occurring in the electrochemical multicycling.

### 3) References

- [1] R. C. Ambrosio and E. A. Ticianelli, *Journal of Electrochemical Society* **2003**, *150*, 438-443.
- [2] S. P. Thompson, J. E. Parker, J. Potter, T. P. Hill, A. Birt, T. M. Cobb, F. Yuan, C. C. Tang, *Review of Scientific Instruments* **2009**, *80*, 075107.
- [3] A. M. WISE, Characterisation of bimetallic alloy and core-shell electrocatalysts, PhD Thesis, University of Southampton, **2012**.
- [4]. R. R. Passos, V. A. Paganin, E. A. Ticianelli, *Electrochim. Acta* *51* (2006) 5239–5245.