Supplementary Material (ESI) for Chemical Communications

More Affordable Electrolytic $LaNi_5$-Type Hydrogen Storage Powders

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ELECTRONIC SUPPLEMENTARY INFORMATION

1. Experimental

The AnalaR grade sub-micrometer powders of La_2O_3 (Sinopharm Group Chemical Reagent Company), NiO (INCO Ltd), Co_3O_4 (Ganzhou Cobalt & Tungsten Company), MnO_2 (Chengdu Shudu Nano-Science Company), Al_2O_3 (Zhengzhou Dayu Chemical Company) and cerium-rich mischmetal oxide (MmO: 28.04 wt% La_2O_3, 51.15 wt% CeO_2, 5.18 wt% Pr_6O_{11}, 15.64 wt% Nd_2O_3, Baotou Hefa Rare Earth Metal Materials Company) were used as-received. The oxide powders were weighed and mixed by ball milling for 6 hours according to the following stoichiometries: $LaNi_5$, $LaNi_4Co$ and $MmNi_{3.55}Co_{0.75}Mn_{0.40}Al_{0.30}$. Typically, at a running speed of 250 r.p.m., the mill was charged with 150 g oxide powder, and 4 large balls (15.00 mm in diameter and 6.500 g in mass), 20 medium balls (10.00 mm, 2.300 g), and 40 small balls (6.00 mm, 0.343 g). About 400 ml anhydrous ethanol was used to assist powder dispersion. It should be pointed out that the milling process was to help uniform mixing of the oxide powders, but other milling settings may also be applied according to our experience. The mixed powders (~2.0 g) were pressed into small cylindrical pellets (diameter 20.1 mm, thickness 2.8 mm) using a hydraulic press at ~6 MPa. The pellets were sintered in air at 500°C-1400°C for 2 h.

Dry molten $CaCl_2$ (AR grade, Shanghai Silian Reagent Company) was used as the electrolyte in the electrolysis experiments. The salt was contained in a graphite crucible (inner diameter, 90.0 mm; height, 235.0 mm) which was placed in a sealable stainless steel reactor in a programmable vertical furnace (Wuhan Experimental Furnace Plant). The furnace temperature was first raised to and maintained at 200 - 300°C for at least 12 h, then to 450°C for 2 h under argon, and finally to the working temperatures (850°C). After melting, pre-electrolysis of the freshly prepared molten salt was applied at 2.6 V to remove moisture and redox-active impurities. A graphite rod (diameter 20.0 mm, length 200 mm) and a molybdenum wire (diameter 2.5 mm) were used as the anode and cathode, respectively. The pre-electrolysis lasted until the current reached a low and stable level. Subsequently, the pellets were wrapped tightly by thin molybdenum wire (100 μm in diameter) into an assembled cathode and inserted in the molten salt to undergo constant voltage electrolysis. After electrolysis the pellets were lifted from the molten salt and cooled in a stream of pure argon gas. Then, the products were washed in distilled water or dimethylsulfoxide (DMSO, 99.9%, Sinopharm Chemical Reagent Co., Ltd) with the aid of an ultrasonic bath, dried in vacuum for 10 h, and characterised by XRD (SHIMADZU X-ray 6000), SEM (HITACHI X-650), ICP-AAS (Agilent 7500a Japan) and Inert Gas Fusion-Infrared Absorption analysis (LECO RO416-DR Analyzer). The XRD patterns of the electrolytic samples are exemplified in **Fig. S1**. The ICP-AAS analysis of the $LaNi_5$ and $LaNi_4Co$ samples indicated the compositions

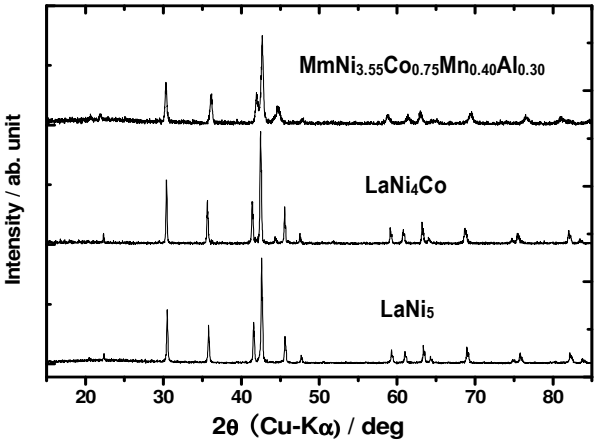


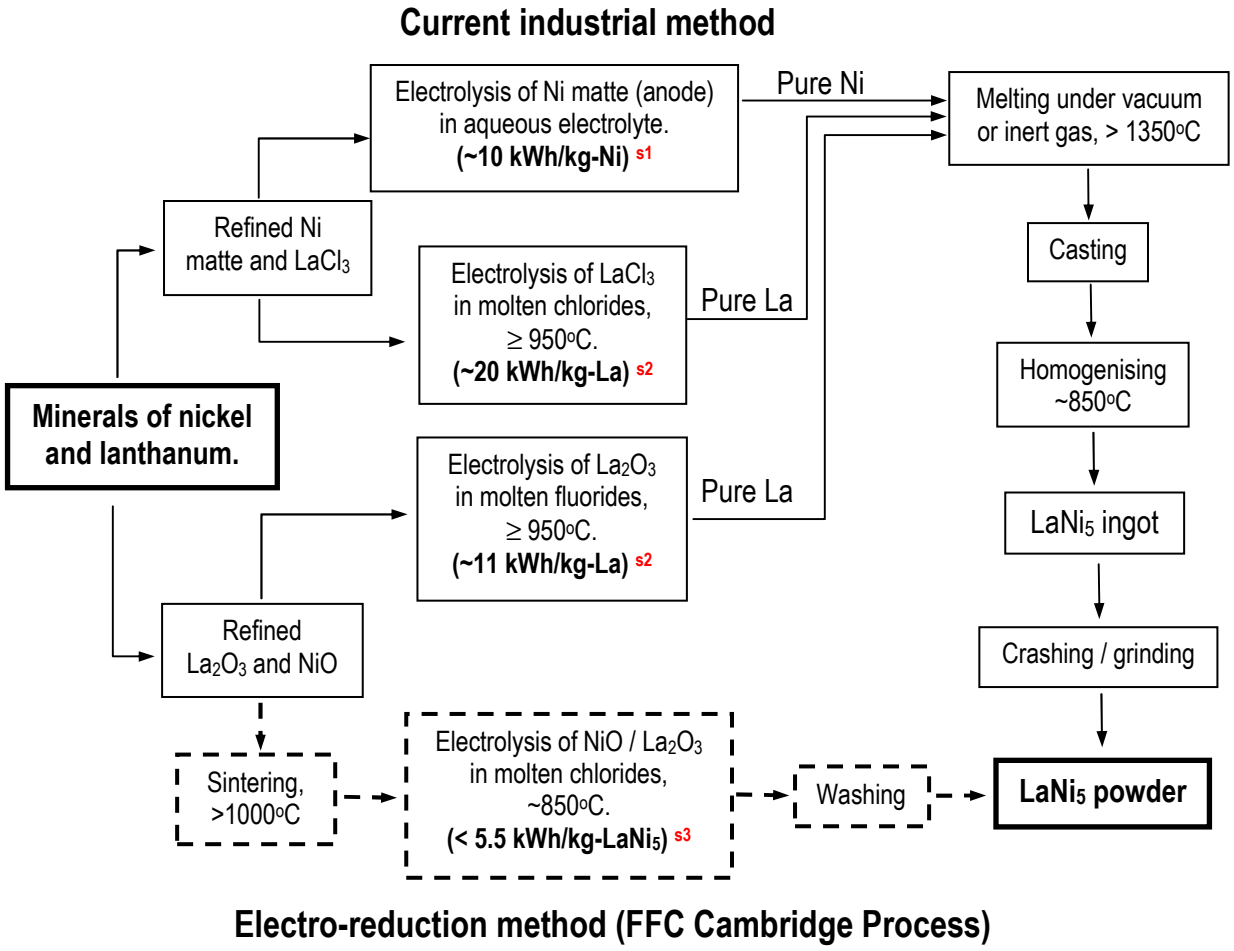
Fig. S1. XRD patterns of the indicated products from electrolysis of the oxide precursors at a cell voltage of 3.1 V for 6 h in molten $CaCl_2$ at 850 °C.

as La/Ni = 1.00/4.67 and La/Ni/Co =1.08/3.80/1.00, respectively. Because the composition of the mischmetal oxide was unknown, the 5-component alloy, $LaNi_{3.55}Co_{0.75}Mn_{0.40}Al_{0.30}$ was prepared for a reference, and the ICP-AAS result was La/Ni/Co/Mn/Al = 1/3.48/0.67/0.41/0.22.

For electrochemical hydrogen storage tests, the electrolytic powder was mixed with nickel powder (INCO Ltd) in a mass ratio of 1:1. A small amount (5 wt%) of polytetrafluoroethylene (PTFE) emulsion was added to the mixture as the binder. The mixture (paste) was then pressed onto a piece of nickel foam (8 mm x 8 mm), followed by drying in vacuum at 80°C for 2 h. The prepared electrodes were each weighed to derive the amount of electrolytic powder, immersed in an electrolyte of 6.0 M KOH at 25°C for at least 1 day to ensure complete wetting, and then subjected to charge/discharge tests with a sintered NiOOH / $Ni(OH)_2$ counter electrode at 60 mA g^{-1} and charge/discharge cut-off voltages of 1.45 V / 0.90 V.

2. Process Flowchart

The following flowchart compares the current industrial method with the electro-reduction method (the FFC Cambridge Process) for the production of the $LaNi_5$ powder. The $LaNi_4Co$ powder may be produced similarly as the extraction of Co also involves electrolysis in aqueous electrolyte.



References

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s2. G. X. Xu, *Rare Earths,* vol. 2, Metallurgical Industry Press, **2002**, 179 (in Chinese).
s3. This work.