

More affordable electrolytic LaNi₅-type hydrogen storage powders†

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Compounding between NiO and La₂O₃ protects the latter from water and molten salt attack, and ensures successful direct electrolytic conversion of the oxide precursors, in the solid state, to more affordable LaNi₅-type hydrogen storage materials.

In response to the growing carbon-strain on the environment, the development of electric vehicles (EVs) (including hybrid ones) with low or zero emission is proceeding at an accelerated pace.^{1a} Up till now, nickel-metal hydride (Ni-MH) rechargeable batteries have been one of the preferred options as the power source for EVs.¹ Metal hydrides (MHs) have been researched since the 1960s.² They are usually environmentally acceptable, and offer high energy and power densities, and long cycle life in the Ni-MH batteries.^{2f} Of all known MHs, the AB₅-types, particularly those derived from LaNi₅, are currently leading the competition.³ However, these materials are still far from being economic for large scale EV applications. This is not because of resource rarity, but largely due to the inadequate manufacturing technologies.†

At present, LaNi₅-type hydrogen storage materials are produced by separate extraction and refining of the individual metals, followed by melting and casting under vacuum.^{4a,b} The cast ingot needs to go through annealing (~850 °C) under vacuum for several hours to eliminate compositional segregation.^{4b} Afterwards, the ingot is made into a powder suitable for making the negative electrode in the batteries by mechanical grinding, hydrogenation–dehydrogenation cycling, or atomisation under an inert atmosphere.^{4b,c,†} Such multi-step processes are high in energy consumption but slow in production, contributing to the relatively expensive commercial Ni-MH batteries that are mostly used in small electronic devices. Obviously, a more cost-effective and novel production method is needed to encourage EV applications.

In the past few years, increasing evidence has shown that metals, particularly the reactive ones, such as Ti and Nb, can be produced by direct electrolytic reduction of the respective solid metal oxides in CaCl₂ based molten salts.⁵ This *electro-reduction* method is lower in energy consumption and simpler in operation than many existing industrial technologies. Its particular advantage lies in the manufacturing of low cost alloys and intermetallics directly from mixed oxide precursors,⁶ but this potential is yet to be demonstrated for producing the highly composition and morphology sensitive LaNi₅-type hydrogen storage powders.

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However, there are expected difficulties in transferring the experimental procedures previously employed for the electro-reduction of transition metal oxides to that of rare earth oxides.⁵ For example, rare earth metals are highly reactive and hence cannot be washed in water, which makes it difficult to separate the electrolytic product from the solidified CaCl₂ salt.^{5h,6e} In particular, La₂O₃ is very hygroscopic, and making the oxide powder into a cathode (*e.g.* porous pellets) is challenging. Unlike many other metal oxides, La₂O₃ can also react with molten CaCl₂ *via* a spontaneous reaction: La₂O₃ + CaCl₂ → 2LaOCl + CaO, ΔG° (850 °C) = -33.538 kJ. This means a greater energy consumption and also possible difficulty in maintaining the cathode's integrity in the molten salt during electrolysis. We have indeed experienced these difficulties in this work but, more importantly, designed a simple procedure to avoid them.

Fig. 1a displays the SEM image of the interior of an as-pressed pellet of mixed NiO and La₂O₃ powders. In this work,† difficulty was encountered in making the La₂O₃ powder into a stable pellet with or without mixing with the NiO powder. The problem was not in the mixing and pressing stages during which the La₂O₃ absorbed moisture from air to be converted fully to La(OH)₃. The absorbed water could be effectively removed by heating in air at temperatures higher than 200 °C. However, once cooled in the ambient environment, the dehydrated pellet absorbed water again and fell apart in a short while. XRD analyses, as shown in Fig. 2a, revealed the La₂O₃ and/or La(OH)₃ phases in all moisture sensitive pellets, disregarding sintering conditions.

The hygroscopic problem was solved by encouraging complete consumption of La₂O₃ in the pellet *via* reaction with NiO and O₂

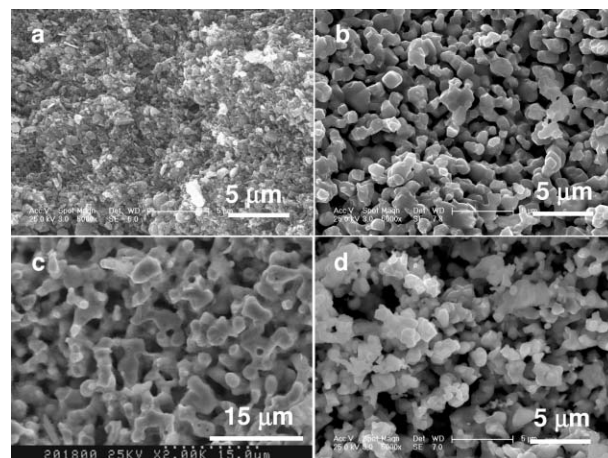


Fig. 1 Scanning electron microscopy. **a.** Mixture of NiO and La₂O₃ powders (La : Ni = 1 : 5 at.). [Ball-milled, pressed and hydrated to La(OH)₃ in air.] **b.** Sintered (a) at 1200 °C for 2 h in air. **c** and **d.** Images taken near the surface (c) and the core (d) of the pellet (b) after electrolysis at 3.1 V in molten CaCl₂ at 850 °C for 6 h.

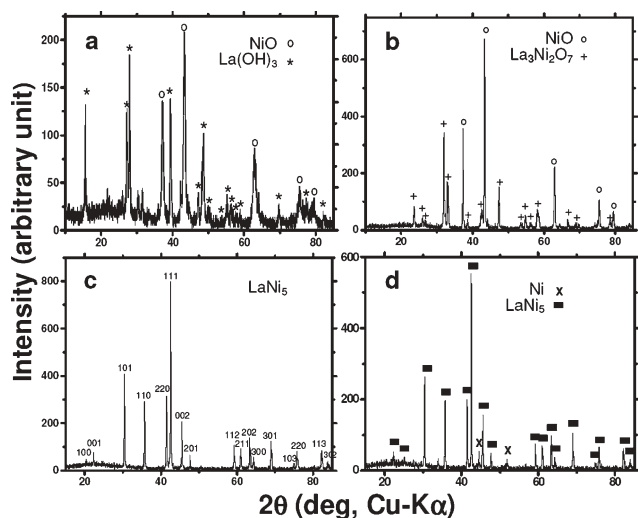


Fig. 2 X-ray diffraction patterns. **a, b.** Same as Fig. 1a and Fig. 1b. **c, d.** Electrolysed at (c) 3.1 V and (d) 2.6 V in molten CaCl_2 at 850°C for 6 h.

to form compounded oxides, *i.e.* the *compounding procedure*.^{6e,f,7a} It was found that pellets sintered in air between $900\text{--}1400^\circ\text{C}$ for 2 h or longer became moisture insensitive. The XRD patterns exhibited no sign of La_2O_3 or $\text{La}(\text{OH})_3$, but evidently one or more of the compounded oxide phases, including LaNiO_3 ($< 1000^\circ\text{C}$), $\text{La}_4\text{Ni}_3\text{O}_{10}$, $\text{La}_3\text{Ni}_2\text{O}_7$ ($1100\text{--}1250^\circ\text{C}$), and/or La_2NiO_4 ($> 1300^\circ\text{C}$).^{6e,7a} Another benefit is that in the compounded phases, the La and Ni atoms are uniformly distributed within a short distance and can react quickly to form the desired alloys or intermetallics once the oxygen atoms are removed at appropriate potentials.^{6e}

Another challenging difficulty was to maintain the integrity of the pellets during electrolysis in molten CaCl_2 . The main cause was thought to be the formation of LaOCl in the pellet as discussed above. The problem was more serious in pellets sintered at lower temperatures (*e.g.* 900°C) but was effectively absent, for example, in the pellets of mixed La_2O_3 and NiO powders (La : Ni = 1 : 5) sintered at 1200°C for 2 h. Under SEM, the growth of the sub-micrometer oxide particles to interconnected micrometer particles was observed clearly, as shown in Fig. 1b. This change strengthened the pellet (but also maintained a porous structure which is beneficial to electro-reduction). On the corresponding XRD patterns, the $\text{La}_3\text{Ni}_2\text{O}_7$ phase was detected in the pellet sintered at 1200°C for 2 h, see Fig. 2b, which can be attributed to the reaction: $6\text{LaNiO}_3 \rightarrow 2\text{La}_3\text{Ni}_2\text{O}_7 + 2\text{NiO} + \text{O}_2$.^{7a} The pellets sintered at temperatures higher than 1300°C contained mainly the La_2NiO_4 phase and were also stable in molten CaCl_2 .

It should be pointed out that the low oxygen partial pressure in the molten salt might have also caused decomposition of the compounded oxide phases, and hence contributed to the observed disintegration of the sintered pellets in molten CaCl_2 . Furthermore, although minor, possible interactions between NiO and the molten salt cannot be excluded at this stage of research.^{6g}

The pellets, each weighing ~ 2.0 g and sintered at 1200°C for 2 h, were electrolysed, as the cathode, at different cell voltages in molten CaCl_2 at 850°C under argon. At 3.1 V, upon applying the voltage, the cell current jumped to a peak with a width of 30 min, as shown in the inset of Fig. 3a. Then, the current showed a slower

decline over about 150 min to a stable level which was maintained until the end of electrolysis. The cell current–time plot recorded at 2.6 V, see Fig. 3b and the inset, exhibits features similar to that in Fig. 3a with slight variations in current and peak position which appears at a later time, meaning a lower reduction rate. From these cell current–time plots, it was estimated that when the voltage was decreased from 3.1 V to 2.6 V, the current efficiency increased slightly from 46.1% to 48.1%, but the energy consumption decreased from $5.38\text{ kWh (kg-LaNi}_5\text{)}^{-1}$ to $4.54\text{ kWh (kg-LaNi}_5\text{)}^{-1}$.

Fig. 1c and 1d show the SEM images taken from the surface and the centre of a pellet electrolysed at 3.1 V for 6 h. While the nodular particles found in the surface layer (Fig. 1c) match well in shape with those of similarly prepared titanium,^{5a,f,g} the significantly smaller size of the particles at the centre (Fig. 1d) suggests their formation later than those in Fig. 1c which results in their not having enough time to sinter into larger particles. The electrolysed pellet could be easily ground into powder with a pestle and mortar without alteration to the morphology shown in Fig. 1c and 1d which is ideal for achieving a high surface-to-volume ratio for hydrogen absorption and also efficient inter-particle pathways for electron conduction. The XRD patterns of the samples obtained by electrolysis at 3.1 V and 2.6 V are presented in Fig. 2c and 2d, respectively. While the 3.1 V pattern agrees very well with the LaNi_5 standard, a small amount of Ni phase can be observed on the 2.6 V pattern. NiO has a more positive reduction potential than that of $\text{La}_3\text{Ni}_2\text{O}_7$. This means that when the applied potential is sufficiently negative to reduce NiO (but not too negative to reduce $\text{La}_3\text{Ni}_2\text{O}_7$), some Ni atoms may form without encountering

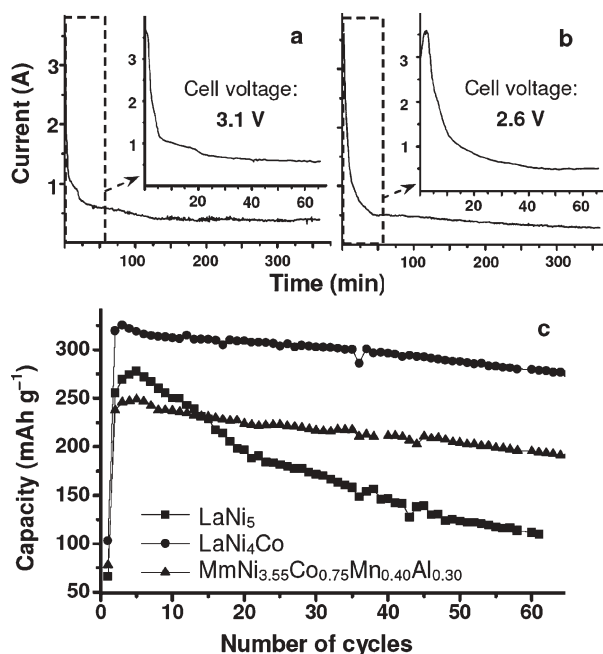


Fig. 3 Electrochemistry. **a, b.** Cell current–time plots of electrolysis of the $\text{La}_2\text{O}_3\text{--NiO}$ pellet (cathode, La : Ni = 1 : 5, 2.0 g, 2.8 mm thickness, 20.1 mm diameter, sintered at 1200°C in air for 2 h, $\sim 45\%$ porosity) at a cell voltage of 3.1 V (a) or 2.6 V (b) in molten CaCl_2 at 850°C . **c.** The discharge capacity variation of the indicated electrolytic LaNi_5 -type powders *versus* the number of charge/discharge cycles (60 mA g^{-1} , 1.45 V/0.90 V) measured in 6.0 M KOH at 25°C .

any nearby La atoms, and hence combine into segregated Ni crystallites. Therefore, a higher voltage would encourage a faster reduction of the $\text{La}_3\text{Ni}_2\text{O}_7$ phase to supply enough La atoms to react with the nearby Ni atoms.

To further confirm the composition of the electrolytic products, ICP-AAS analysis was performed, showing an atomic ratio of $\text{La}/\text{Ni} = 0.21$, but no other impurity in the sample. The slightly lower Ni content in the sample agrees with what was found in similarly prepared TbNi_5 , suggesting possible interactions between NiO and molten CaCl_2 that deserve further investigation.^{6f,g} The oxygen content in the electrolytic powder was measured on the LECO analyzer to be 10000 ppm and 6000 ppm for samples washed in water and DMSO, respectively. The actual oxygen content in the as-electrolysed sample may be lower because the LaNi_5 particles could have been oxidised on the surface after exposure to air and going through the washing procedure.

Electrolysis of the pellets sintered under other conditions was also attempted. When sintering below 1000 °C, the pellets were unstable in molten CaCl_2 , leading to material loss after electrolysis. Between 1000 °C and 1200 °C, XRD revealed the LaOCl phase in partially electrolysed products. Electrolysis of the La_2NiO_4 phase dominated pellets for 6 h only led to surface metallisation, apparently due to the much greater density in these high temperature sintered pellets. Unlike those pellets sintered at lower temperatures, the LaOCl phase was not observed in the unreduced pellet core which remained in the compounded oxide phase.

It is known that the intrinsic LaNi_5 compound can be improved for electrochemical hydrogen storage performance, e.g. charge–discharge cycling, by partial substitution of Ni with Co, Mn and/or Al. To confirm the same effect on the electrolytic product, LaNi_4Co and $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.40}\text{Al}_{0.30}$ (Mm: mischmetal) were prepared similarly from the respective oxide powder mixtures. The as-prepared electrolytic powders were made directly into the cathode and tested in a laboratory Ni-MH battery.† Fig. 3c plots the discharge capacity of each sample against the number of charge–discharge cycles at 25 °C. All plots show an initial steep increase to a maximum, corresponding to the activation process, followed by an almost linear decay. It can be seen that the LaNi_4Co electrode reaches 325 mAh g^{-1} after 3 activation cycles and slowly decreases to 280 mAh g^{-1} after 60 charge–discharge cycles. The electrode of $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.40}\text{Al}_{0.30}$ shows a peak capacity of 249 mAh g^{-1} after 5 cycles and only decreases to 195 mAh g^{-1} after 60 cycles. As expected, the LaNi_5 exhibits an inferior cycling performance with the capacity decreasing from a maximum of 278 mAh g^{-1} after 5 activation cycles to only 112 mAh g^{-1} after 60 cycles.

The theoretical electrochemical hydrogen storage capacity for charging LaNi_5 to LaNi_5H_6 ^{1a} is 371.9 mAh g^{-1} , which is not too far away from the maximum discharging capacities measured from the electrolytic LaNi_5 and LaNi_4Co powders. In fact, the whole picture of the electrochemical hydrogen storage performance shown in Fig. 3c compares very well with that of the same or similar LaNi_5 -type materials prepared by other methods.^{2d,f,3d,4b} However, the electro-reduction process not only is simpler and faster in operation, but also incurs less electrolysis energy [below 5.5 kWh (kg-alloy)⁻¹]. In the current industry, the energy consumption for the extraction of Ni is at ~ 10 kWh (kg-Ni)⁻¹ (electrolysis in an aqueous bath),^{7b} and that of La at 11–20 kWh (kg-La)⁻¹ (electrolysis in molten salts).^{7c} These data

correspond to 10.3–13.2 kWh (kg- LaNi_5)⁻¹ for the pure metals. Further energy consumption is inevitable when the pure metals are made into the alloy powder *via* melting (Ni melts at 1455 °C, La at 920 °C, and LaNi_5 at 1350 °C), casting, homogenising (~ 850 °C), and grinding. In fact, our electrolysis energy consumption is even lower than that for making the cheapest commercial metal, crude steel [greater than 5.5 kWh (kg-steel)⁻¹].^{7d} While the research is still ongoing for better fundamental understanding and technical optimisation (e.g. to increase the current efficiency), the preliminary results, in particular the *compounding procedure*, reported here demonstrate the great potential of using the electro-reduction method for the commercial production of more affordable LaNi_5 -type hydrogen storage materials.

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