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Rechargeable Ni-Li Battery Integrated Aqueous/Nonaqueous System

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Climate change and exhaust of fossil fuels drive the increasing worldwide interest in the development of electrochemical power sources for diverse applications from cell phones to electric vehicles. Currently, efforts in battery research and development are devoted to energy storage and conversion with high energy density, high power density, and reliable safety.[1]

The amount of electrical energy E (Wh/kg) that a battery is able to deliver is a function of the cell voltage U (V) and capacity Q (Ah/kg), both of which are linked directly to the chemistry of the system. Even the prominent battery technologies, such as the Li-ion battery and Ni-MH battery, still demonstrate huge gaps between expected and practical performances. The Li-ion battery, profiting from the adoption of an organic electrolyte whose wide stable electrochemical window allows utilization of both high potential and low potential electrodes, holds a theoretical cell voltage as high as 4.10 V (Figure 1a). However, it falls short with the limited inherent capacity of its cathode materials.[2] $Li_{1-x}CoO_2$ ($x \leq 0.5$), the current dominant cathode material, can only exhibit a reversible capacity up to 137 mAh/g in comparison with 372 mAh/g for the graphite anode. Another challenge regarding the Li-ion battery is the low power density, which is restricted by the slow electrode kinetics relating to Li intercalation/deintercalation from its host materials.[1d] Also, safety is always a big concern for Li-ion batteries especially in terms of large-scale application as in hybrid electric vehicles.[1d] The highly delithiated state of the cathode material might release oxygen, which can cause severe thermal runaway reactions leading to fire or explosion of the cell.[3] $LiFePO_4$, with a lower redox potential as well as better thermal stability, thus attracted more attention in recent years and is considered as the most promising cathode material for next generation Li-ion batteries.[4] It can deliver a capacity of 170 mAh/g, still poor compared to the capacity of the cathode material in a Ni-MH battery, e.g. 289 mAh/g for β-$Ni(OH)_2$. Shifting the battery system from a flammable organic electrolyte to an aqueous electrolyte would intrinsically increase the safety but at the expense of low cell voltage due to the narrow allowable voltage window of water.[5] As for the Ni-MH battery, both its cathode and anode material are able to deliver a large capacity, e.g. 298 mAh/g for β-$Ni(OH)_2$ and 340 mAh/g for typical metal hydride $LaNi_5H_x$ ($x \leq 6$). However, its cell voltage is only 1.32 V (Figure 1b) due to the limitation of aqueous electrolyte. So, is there any solution which can simultaneously deliver a high cell voltage like the Li-ion battery and a large cell capacity like the Ni-MH battery?

One radical exploration is to break the routine of classical batteries which involves a single electrolyte. If an aqueous electrolyte and organic electrolyte can be smartly integrated in one battery, it would enable state-of-the-art combination choices for the existing battery chemistry. Recently, a superionic conductor glass ceramic film (LISICON) with stability in aqueous solution and its application in a Li-air battery has been reported.[6] Here, we proposed integrating a nickel hydroxide electrode working in an aqueous solution as the cathode and a Li metal working in an organic electrolyte as the anode by a LISICON film to fabricate a rechargeable Ni-Li battery (Figure 1c). Li is the most negative metal while at the same time possessing an ultrahigh capacity of 3860 mAh/g, thus facilitating the design for high energy density. However, the uneven plating of Li in the form of dendrites during discharge−recharge cycles may puncture the polyolefin thin separator, leading to short circuit hazards. In the Ni-Li battery, the rigid ceramic LISICON film is hardly punctured by Li dendrites thus enabling the utilization of Li metal. As for a cathode electrode, nickel hydroxide, with a less positive potential and an aqueous solution as the electrolyte, is inherently safer than the case of the cathode in the Li-ion battery. More importantly, the proposed Ni-Li battery promises both a high cell voltage (3.49 V) and a large cell capacity (268 mAh/kg), which together endows an ultrahigh energy density; e.g. the theoretical energy density regarding only the active electrodes and cell voltage is calculated to be 414, 214, and 935 Wh/kg for the Li-ion, Ni-MH, and Ni-Li batteries, respectively.

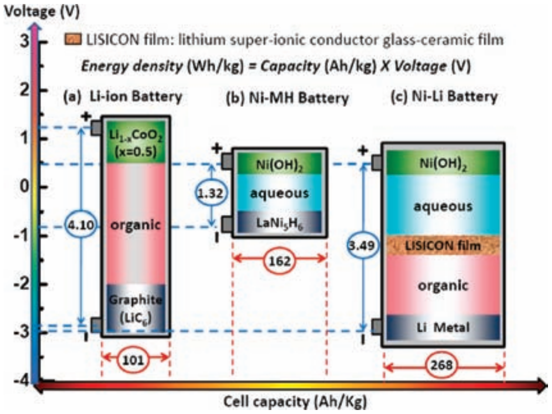

Figure 1. Key components, cell voltage, and cell capacity of Li-ion battery (a), Ni-MH battery (b), and the proposed Ni-Li battery (c). The cell capacity (Q) is calculated by $Q = Q_+/(1 + Q_+/Q_-)$, where Q_+ and Q_- is the theoretical capacity of cathode material and anode material, respectively.

A prototype Ni-Li battery was assembled by using 1 M $LiClO_4$ in ethylene carbonate/dimethyl carbonate as the electrolyte for the Li anode and an aqueous solution containing 1 M LiOH and 1 M KOH as the electrolyte for the $Ni(OH)_2$ cathode. The two electrolytes were separated by a water-stable LISICON film ($Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$, provided by Ohara Inc., Japan) with a thickness of 0.15 mm. Co-coated β-$Ni(OH)_2$ powder (see XRD pattern in Figure S1) was provided by Tanaka Chemical Corporation. The cathode electrode (∼0.80 mg, ∼0.5 cm × 0.5 cm in area) consisted of 75% $Ni(OH)_2$, 20% carbon black, and 5% poly(tetrafluoroethylene) (PTFE). Li metal with a larger area than the cathode (excessive in amount) was used as the anode. The chemical reaction within the Ni-Li battery can be described in the following:

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$$(+): \mathrm{Ni(OH)_2} + \mathrm{OH^-} - \mathrm{e^{-1}} \leftrightarrow \mathrm{NiOOH} + \mathrm{H_2O}\ (\varphi = 0.49\ \mathrm{V}) \quad (1)$$

$$(-): \mathrm{Li^+} + \mathrm{e^{-1}} \leftrightarrow \mathrm{Li}\ (\varphi = -3.00\ \mathrm{V}) \quad (2)$$

$$\text{Overall: } \mathrm{Ni(OH)_2} + \mathrm{LiOH} \leftrightarrow \mathrm{NiOOH} + \mathrm{Li} + \mathrm{H_2O} \quad (3)$$

In the discharge process, β-NiOOH is reverted to β-$Ni(OH)_2$ and the Li-anode is converted to Li ions, the formed Li ions diffuse from the nonaqueous electrolyte to an aqueous electrolyte through a LISICON film, while at the same time, electrons pass the external circuit; the charge process undergoes a reverse mechanism. It should be noted that only lithium ions can pass across the LISICON film during a charge/discharge process.

The typical charge/discharge curves of the Ni-Li battery was shown in Figure 2a. At a discharge current density of 0.1 A/g, it exhibited a capacity of 264 mAh/g, nearly 91% of the theoretical capacity of β-$Ni(OH)_2$. The discharge capacity at higher current density, e.g. 0.2, 0.5, and 1.0 A/g, was 261, 246, and 215 mAh/g, respectively, demonstrating a good retention of the initial capacity. However, a steady decay of cell voltage was also observed with the increase of discharge rate, which was mainly due to the large resistance of the LISICON film. The detected iR drop ($\triangle V$) at the initial stage of discharge increased from 0.04 to 0.20 V when the discharge current was increased from 0.1 to 1.0 A/g; accordingly, the discharge plateau (see dashed arrow across discharge curves in Figure 2a) declined from 3.47 to 3.24 V, respectively. The energy density of this cell was estimated as 857 Wh/kg by using the cell voltage and cell capacity (based on the weight of active $Ni(OH)_2$ and Li in electrodes) at 0.1 A/g. In general, the active electrode weighed ~50% of the total weight of practical cells, if the Sony Li-ion product is used as an example.[5b] Then a practical energy density near 428 Wh/kg can be expected for this cell chemistry. The internal resistance of the developed Ni-Li battery was regarded as 67 Ω according to the intercept of an impedance spectrum (Figure S2) on the real axis at high frequency. In comparison, the LISICON film itself demonstrated a similar bulk resistance (also obtained by impedance measurement) when immersed in different solutions, as reported by Hasegawa et al.[6a] The decay of cell voltage was somewhat larger compared to the iR drop, e.g. 0.23 vs 0.16 V, since the actual working process of a battery was known to experience much more complex polarization in addition to the part that arose from internal resistance. Figure 2b showed the cycle performance of the Ni-Li battery at a constant charge/discharge current of 0.2 A/g. The capacity increased in the first several cycles due to the activation of β-$Ni(OH)_2$ and then slightly decayed during the subsequent decades of cycles. It remained at a capacity of 256 mAh/g after 50 cycles of charge/discharge. The coulomb efficiency of the first cycle was ~86% and then increased to 94% for the eighth cycle. It remained nearly stable at 95%−96% during the following cycles.

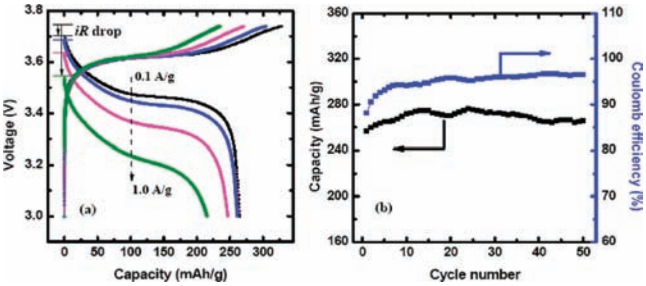

Figure 2. Typical charge/discharge curves and cycle performance of the prototype Ni-Li battery between 3 and 3.75 V; the capacity is based on the mass of $Ni(OH)_2$ in cathode electrode. (a) The cell was charged at 0.1 A/g and discharged at 0.1, 0.2, 0.5, and 1.0 A/g, respectively. (b) The cell was charged and discharged with a constant current of 0.2 A/g.

The above preliminary results demonstrated the feasibility of a rechargeable Ni-Li battery. Obviously, opportunities and challenges coexist in this new type of system. The capacity of cathode material, which currently determines the total cell capacity, can be promoted by adopting the α-$Ni(OH)_2$/γ-NiOOH couple. The nickel oxidation state in γ-NiOOH is known to be 3.33 due to the Ni^{4+} defects and,[7] thus, can yield more than one electron transfer during charge/discharge. A large and stable capacity of 391 mAh/g has been reported for Al-substituted α-$Ni(OH)_2$.[8] The power ability of the Ni-Li battery is expected to be superior to that of the Li-ion battery regarding the electrode kinetics. The current data are not satisfying due to the low conductivity of the LISICON film (~10^{-4} S/cm). For the sake of safety, good mechanical strength and long durability are also highly demanded for the LISICON film so that it can ensure a reliable separation of the two electrolytes during the lifetime of the battery. Although it seems somewhat complicated to assemble such a type of battery, the implementation of a hybrid electrolyte can provide a variety of choices for electrode materials; e.g., AgO with a larger capacity and PbO_2 with a higher potential can also serve as the cathode.

In summary, we propose a rechargeable battery system by integrating two reversible electrode processes associated with an aqueous and a nonaqueous electrolyte, respectively. The prototype Ni-Li battery promised an ultrahigh theoretical energy density as well as a high power potential, which reinforced the view that it is an important avenue to fulfill the best-performing combination for an electrode/electrolyte/electrode system.

Supporting Information Available: XRD pattern of the commercial β-$Ni(OH)_2$ powder (Figure S1); Impedance spectrum of the prototype Ni-Li battery (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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