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Investigation on substrates of $MmNi_5$-based alloy electrodes for high power applications

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Abstract

A new substrate (quasi-3D) combined with both three-dimensional (3D) and two-dimensional (2D) networks for $MmNi_5$-based alloy electrodes was developed. The substrate effect on electrode packing density, porosity, loading capacity, electrode thickness, α ($=W_s$ (substrate weight)/W_e (electrode weight)) and rate capability has been investigated to compare with conventional foamed nickel (3D) and punching metal (2D). The results showed that thin electrodes with punching metal substrates had better rate capability than those with foamed nickel substrates, while both kinds of the substrates had low packing density. Further results indicated that under the condition of the similar electrode thickness, the electrode using the new developed (quasi-3D) substrate showed better performance than those with punching metal and foamed nickel substrates, and could simultaneously keep high packing density and rate capability. It is suggested that this new developed substrate is more suitable for high power applications in nickel/metal hydride batteries.

Keywords: Substrate; $MmNi_5$-based alloy; Nickel/metal hydride battery; High power application

1. Introduction

The global concerns over air pollution and depletion of natural petroleum urge people to renew the interest in hybrid electric vehicles (HEVs). Since Toyota launched its first HEV "Prius" as the world's first commercialized hybrid passenger car in 1997 [1], much attention has been paid [2–8]. Subsequently, Toyota put its "New Prius" with the high fuel efficiency of 35.5 km/l into the market on 1 September 2003 [9]. However, the final acceptance of HEVs will strongly depend on the power performance and the cost of the onboard batteries. Among the present battery systems, nickel/metal hydride (Ni/MH) battery is the most promising one in the near future [3,8].

Most of the previous reports on Ni/MH batteries were concentrated on how to increase the capacity of hydrogen storage alloys in negative electrodes [10]. However, rate capability is the most important for high power applications. In such cases, Ni/MH batteries normally compose of thin electrodes in order to keep high power performance, in which negative electrodes are composed of alloy powders and substrates. Although most efforts have focused on the optimism of alloys' composition and surface treatment of alloys [10], our recent work showed that it was not enough to improve power performance [11]. Therefore, the substrate as one part of the negative electrode was put forward to improve the rate capability of the negative electrode. However, according to our knowledge, although there are many papers on MH electrodes [10], few of them have investigated the effect of substrates on the electrode performance.

The moderate design of the substrate allows optimization of the current distribution, achievement of the maximum value of active material utilization and housing of active materials in the electrode over a long service life. However, the process of selection of the substrate design is extremely difficult due to the fact that compliance with one set of requirements often contradicts the conditions for optimization of another set of requirements. It will be coincided in the case of thin MH electrodes for high power applications. When designing such a high-powered Ni/MH battery, it is tempting to use a thin MH electrode as it increases the high power capability. However, this is done at the expense of packing density. In order to keep high energy density and high rate capability simultaneously, the substrate should be designed properly.

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So far, several types of substrates for MH electrodes have been reported. In the early days of the development of Ni/MH batteries, foamed nickel with a three-dimensional (3D) network as the supporting framework [12,13] was very popular as the substrate of MH electrodes. Later, punching metal with a two-dimensional (2D) network as the supporting framework gradually replaced foamed nickel as the substrate of MH electrodes due to the better conductivity of alloy powders [14]. Foamed nickel was very efficient to house active material and keep high rate capability. However, its cost was too high. Although its cost was lower than that of foamed nickel, punching metal had some difficulty in keeping high capacity and rate capability simultaneously.

In this paper, in order to find a suitable candidate of substrates for high power applications, a new substrate combined with both 3D and 2D networks with low cost was developed. This new substrate effect on packing density, porosity, loading capacity, electrode thickness, α ($=W_s$ (substrate weight)/W_e (electrode weight)) and rate capability was compared with that of the conventional foamed nickel (3D) and punching metal (2D) substrates.

2. Experimental

An $MmNi_5$-based ($CaCu_5$-phase structure) alloy, $MmNi_{4.2}Co_{0.3}Mn_{0.4}Al_{0.3}$ [11], prepared by induction melting with a capacity of about 300 mAh/g was chosen as an active material of MH electrodes. The average particle size of the alloy was about 20 μm, which was determined by a Shimadzu SK-LMS PRO-7000S laser particle size analyzer. The electrodes were prepared as followed: 95 wt.% alloy powder was well mixed with 5 wt.% Ni powder (Inco 255) together with PVA (2 wt.% aqueous solution) as a binder. This mixture was pasted into/onto each substrate, and pressed to form a plate by roller press. Two samples for each type substrate were tested in order to check the reproducibility.

Packing density, porosity, loading capacity, electrode thickness, α ($=W_s$ (substrate weight)/W_e (electrode weight)) and rate capability of the electrodes with the different substrates were examined in a 30% (w/w) KOH + 30 g/l LiOH electrolyte in unsealed cells at 25 °C. Those electrodes described above were used as negative ones in those cells. Conventional sintered $NiOOH/Ni(OH)_2$ plates were used as positive electrodes. Each alloy electrode was placed in the central compartment and two pieces of sintered Ni electrodes with the same size were placed on either side. A sulphonated polypropylene non-woven separator used in commercial batteries was used to separate the positive and negative electrodes.

During activation process, each cell was charged at 0.2*C* (60 mA/g) for 6 h followed by 30 min rest, then discharged at 0.3*C* (90 mA/g) to 1 V cutoff. In order to make it completely activated, the cell was charged and discharged for 15 cycles. The rate capability was evaluated by charging at 0.2*C* for 6 h and discharging at 0.2*C*, 1*C*, 3*C*, 5*C* and 10*C* with the cutoff voltage 1.0, 1.0, 0.8, 0.6 and 0.5 V, respectively. All the charge and discharge tests were performed using a computer controlled charge/discharge system (Keisokuki Center BS2500).

3. Results and discussion

3.1. Different substrates for MH electrodes

Fig. 1 shows the optical images of several types of substrates for MH electrodes. Substrates a and b were punching metals (2D), where b had a lighter weight per unit area and larger pores than a. Substrate c was an Ni sheet with the porosity of 30.0%. Substrates d and e were foamed nickel (3D), where e had a lighter weight per unit area and larger pores than d. Substrate f was the new developed substrate, which had a quite different structure from foamed nickel and punching metal. Because it was composed of both 3D and 2D structures, f was actually considered as a quasi-3D structure. The detailed information on the different substrates is shown in Table 1.

3.2. MH electrodes with 2D substrates

3.2.1. Loading properties

Table 2 shows the loading properties of the electrodes with punching metal (a and b) and Ni sheet (c) substrates. It can be clearly seen that the difference in α values was not so significant. The packing density of MH electrodes was increased from 4.43 g/cm^3 (c) and 4.84 g/cm^3 (b) to 5.48 g/cm^3 (a) with the increase of the electrode thickness from 0.220 mm (c) and 0.275 mm (b) to 0.332 mm (a). The porosity of each electrode was decreased from 35.4% (c) and 30.9% (b) to 22.4% (a).

The loading capacity based on the MH alloy weight was almost the same. It was around 300 mAh/g. Moreover, the difference in the loading capacity based on the electrode weight was also not so significant due to the little difference in α. The capacity based on electrode weight was 257 mAh/g (c), 270 mAh/g (b) and 262 mAh/g (a), corresponding to $\alpha =$ 0.15 (c), 0.12 (b) and 0.13 (a), respectively. However, the loading capacity based on the electrode volume was quite different, which was increased with the rise of the packing

Table 1
Characteristics of punching metal (2D), foamed nickel (3D) and the new developed (quasi-3D) substrate for MH electrodes

Substrate	Unit weight (g/m^2)	Thickness (mm)	Porosity (%)
(a) Punching metal (2D)	255	0.07	36.2
(b) Punching metal (2D)	192	0.06	55.9
(c) Ni sheet (2D)	214	0.03	30.0
(d) Foamed nickel (3D)	370	1.60	93.0
(e) Foamed nickel (3D)	259	0.47	93.8
(f) New substrate (quasi-3D)	275	0.45	93.1

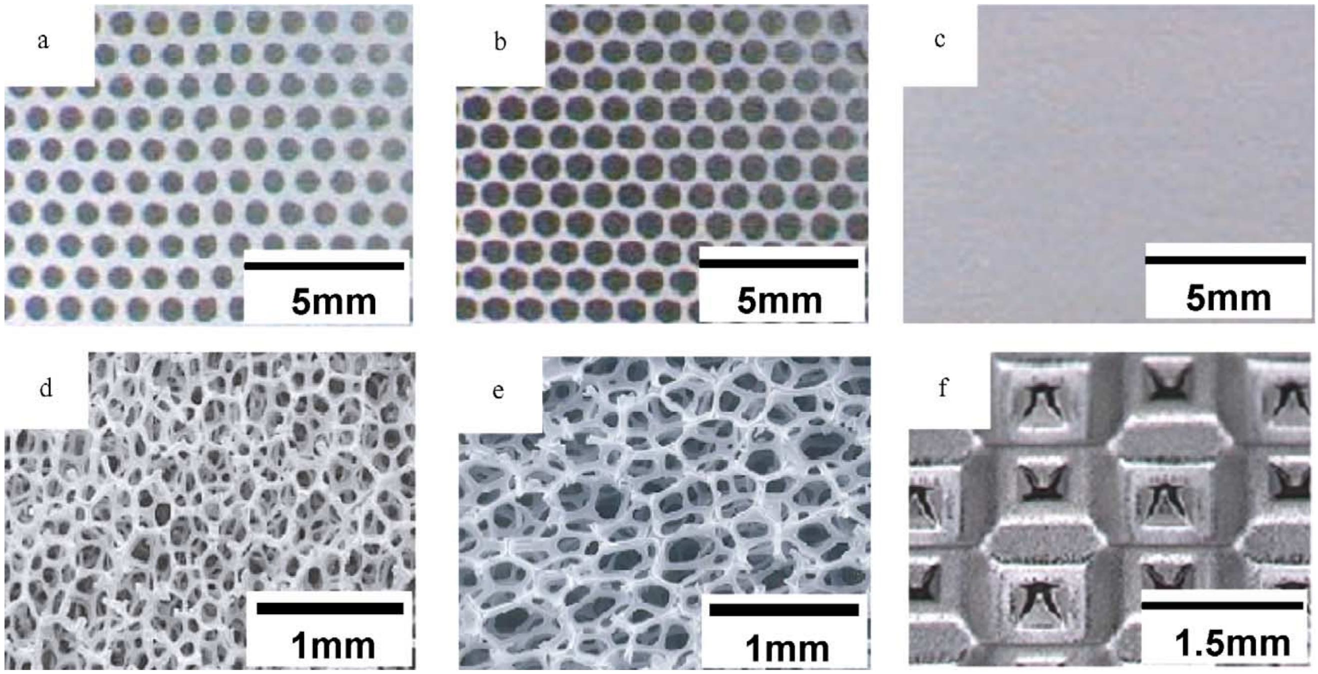

Fig. 1. Optical images of the substrates for MH electrodes: (a and b) punching metal (2D); (c) Ni sheet; (d and e) foamed nickel (3D); (f) new substrate (quasi-3D).

density (or the drop of the porosity). It was 1339 mAh/cm^3 (c), 1493 mAh/cm^3 (b) and 1645 mAh/cm^3 (a), corresponding to packing density of 4.43 g/cm^3 (c, 35.4%), 4.84 g/cm^3 (b, 30.9%) and 5.48 g/cm^3 (a, 22.4%), respectively. This implied that the packing density (or porosity) had a positive (or negative) effect on the loading capacity of the MH electrodes with 2D substrates.

3.2.2. Rate capability

The rate capability of the electrodes with substrates a–c is shown in Fig. 2. It can be seen that at each discharge rate, the electrode with the substrate c showed higher discharge capacity than those with the substrates a and b, while the electrode with the substrate b had higher discharge capacity than that with the substrate a. The electrode with the substrate a with the highest thickness showed the lowest discharge capacity. At 10*C* rate, the discharge capacity of the electrodes was 128 mAh/g (a), 206 mAh/g (b) and 223 mAh/g (c), respectively.

From Table 2 and Fig. 2, it can be found that with the rise of the packing density, the rate capability based on alloy powder weight was decreased. At 10*C* rate, the discharge capacity was 223 mAh/g (c, 4.43 g/cm^3) and 206 mAh/g (b, 4.84 g/cm^3), respectively. For the electrode with the substrate a (5.48 g/cm^3), it was 128 mAh/g. In normal cases, the discharge capacity should be increased with the rise of the packing density due to the compact contact among alloy powders. Then, it implied that the packing density had little effect on the rate capability of the electrodes with 2D substrates. There should be other factors affecting the rate capability.

Table 2
Loading properties of MH electrodes with punching metal (2D), foamed nickel (3D) and the new developed (quasi-3D) substrate (25 °C)

Type	Substrate						
	a	b	c	c-1	d	e	f
Electrodes							
Thickness (mm)	0.332	0.275	0.220	0.285	0.256	0.270	0.290
Packing density (g/cm^3)	5.48	4.84	4.43	5.04	4.17	4.70	5.33
Porosity (%)	22.4	30.9	35.4	28.9	29.6	28.9	23.6
$\alpha = W_s/W_e$[a]	0.13	0.12	0.15	0.13	0.28	0.18	0.15
Loading capacity							
mAh/g (alloy)	301	306	302	300	298	294	298
mAh/g (electrode)	262	270	257	264	218	237	253
mAh/cm^3	1645	1493	1339	1522	1242	1390	1590

[a] Where W_s and W_e are weights of substrate and electrode in an electrode, respectively.

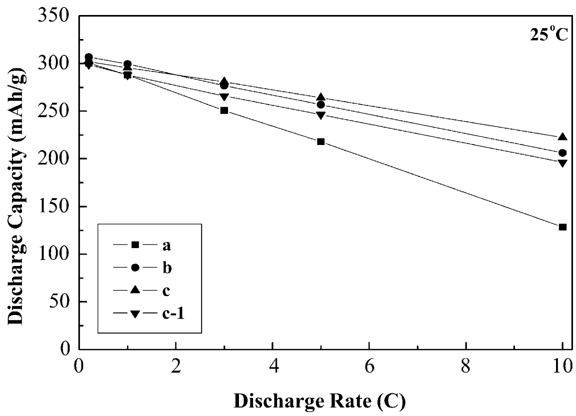

Fig. 2. Rate capability based on alloy powder weight of electrodes with 2D substrates as a function of discharge rates (25 °C): (a) punching metal, $\alpha = 0.13$, 0.332 mm, 5.48 g/cm^3; (b) punching metal, $\alpha = 0.12$, 0.275 mm, 4.84 g/cm^3; (c) Ni sheet, $\alpha = 0.15$, 0.220 mm, 4.43 g/cm^3; (c-1) Ni sheet, $\alpha = 0.13$, 0.285 mm, 5.04 g/cm^3.

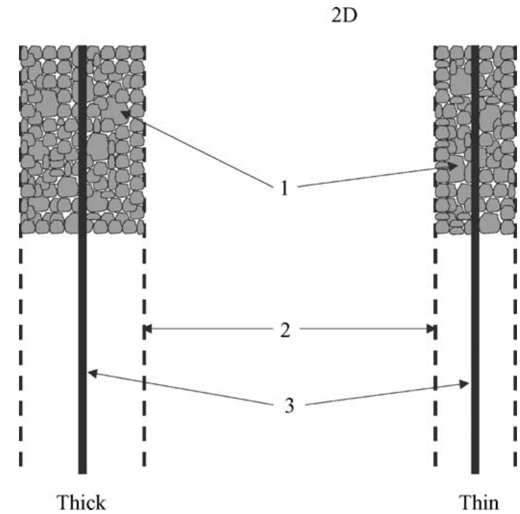

Fig. 4. Illustration of the cross-section of the electrodes with 2D substrates: (1) alloy or Ni particle; (2) one side of MH electrode; (3) framework of substrate.

Fig. 3 shows the relationship between the discharge capacity at 10*C* rate and the electrode thickness of the electrodes with substrates a–c. It can be found that with the drop of the electrode thickness from 0.332 mm (a) to 0.220 mm (c) the discharge capacity was increased from 128 mAh/g (a) to 223 mAh/g (c). It indicated the high rate capability was more sensitive to the electrode thickness for 2D substrates. In order to further check the electrode thickness effect, another electrode, named as c-1 using the same substrate with c was introduced.

The detailed information of the electrode with the substrate c-1 was shown in Table 2. Compared with that using the substrate c, the electrode with the substrate c-1 had a higher electrode thickness. It was 0.285 mm, while that of the electrode with the substrate c was 0.220 mm. The packing density was 4.43 g/cm^3 (c) and 5.04 g/cm^3 (c-1), respectively.

Fig. 2 also shows the rate capability of the electrode with the substrate c-1 at different rates. It can be seen that at each discharge rate, the electrode with the substrate c-1 (0.285 mm) showed lower discharge capacity than that with the substrate c (0.220 mm). At 10*C* rate, the discharge capacity was 223 mAh/g (c) and 197 mAh/g (c-1), respectively. It proved that electrode thickness had a more important effect on the high rate capability than the packing density for the 2D substrates.

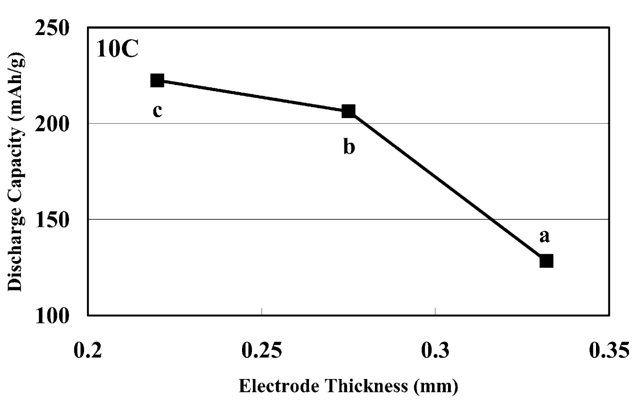

Fig. 3. Relationship between discharge capacity at 10*C* rate and electrode thickness of electrodes with 2D substrates: (a and b) punching metal; (c) Ni sheet.

Fig. 4 shows the illustration of the cross-section of the electrodes with the 2D substrates. It was evident that the thin electrode had better conductivity between the active material and the substrate due to the short distance between the substrate framework and the edges of the electrode. Then, the electrodes with the thinner thickness had better rate capability. However, under such conditions, the packing density was very low as shown in Table 2.

3.3. MH electrodes with 3D substrates

Table 2 also shows the loading properties of the MH electrodes with the foamed nickel (d and e) substrates. The influence of the α on the electrode properties was very significant unlike the punching metals. With the drop of α from 0.28 (d) to 0.18 (e), the packing density was increased from 4.17 g/cm^3 (d) to 4.70 g/cm^3 (e), and the loading capacity based on the electrode weight was increased from 218 mAh/g (d) to 237 mAh/g (e). It implied that the unit weight of the substrate should be reduced as much as possible in the case of the loading capacity for foamed nickel. It can be also found that the loading capacity based on electrode volume was increased with the rise of packing density. It was 1242 mAh/cm^3 (d) and 1390 mAh/cm^3 (e), corresponding to 4.17 g/cm^3 (d) and 4.70 g/cm^3 (e), respectively. It implied that the packing density had a positive effect on the loading capacity.

Fig. 5 shows the rate capability of the electrodes with the foamed nickel (d and e) substrates. It can be seen that the

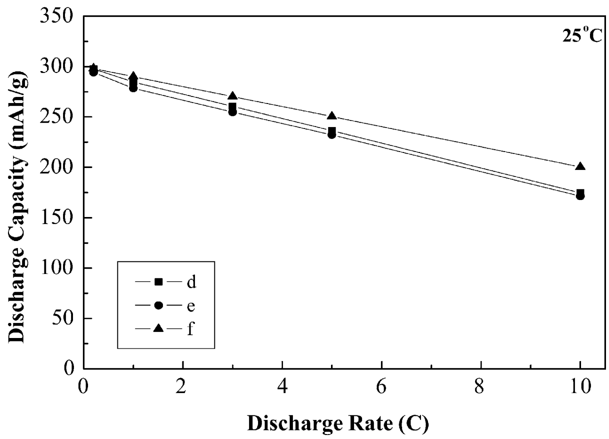

Fig. 5. Rate capability based on alloy powder weight of the electrodes with 3D and quasi-3D substrates as a function of discharge rates (25 °C): (d) foamed nickel (3D), $\alpha = 0.28$, 4.17 g/cm^3, 29.6%; (e) foamed nickel (3D), $\alpha = 0.18$, 4.70 g/cm^3, 28.9%; (f) new developed substrate (quasi-3D), $\alpha = 0.15$, 5.33 g/cm^3, 23.6%.

electrode with the substrate d had slightly better rate capability than that with the substrate e. At 10*C* rate, the discharge capacity was 174 mAh/g (d) and 171 mAh/g (e), while the packing density was 4.17 g/cm^3 (d) and 4.70 g/cm^3 (e), respectively. It also proved the fact that keeping high packing density always contradicted keeping high rate capability for the foamed nickel substrates.

In order to find a suitable substrate for high power applications, the new substrate (quasi-3D) combined both 2D and 3D networks was developed and compared with the conventional punching metal and foamed nickel.

3.4. MH electrodes with the new developed (quasi-3D) substrate

3.4.1. Loading properties

Table 2 also shows the information on the electrode with the new developed substrate f (quasi-3D). Compared with 3D substrates, the electrode with the quasi-3D substrate had much better loading properties, e.g. higher packing density (5.33 g/cm^3) and lower α (0.15), which behaved like 2D ones. Furthermore, it can be also found that under the condition of the similar electrode thickness, the loading capacity of the electrode with the quasi-3D substrate was slightly higher than those of the electrodes with the 2D substrates. For example, the electrode with the substrate f had a higher value than that with the substrate c-1. It was 1590 mAh/cm^3 (f) and 1522 mAh/cm^3 (c-1), while the electrode thickness was 0.290 mm (f) and 0.285 mm (c-1), respectively. It implied that the electrode with the quasi-3D substrate had a superior loading capacity to those with the 2D and 3D substrates.

3.4.2. Rate capability

Fig. 5 also shows the discharge capacity of the electrode with the quasi-3D substrate f at different rates. It can be found that this electrode had much higher discharge capacity than those with the 2D substrates (d and e) at each rate.

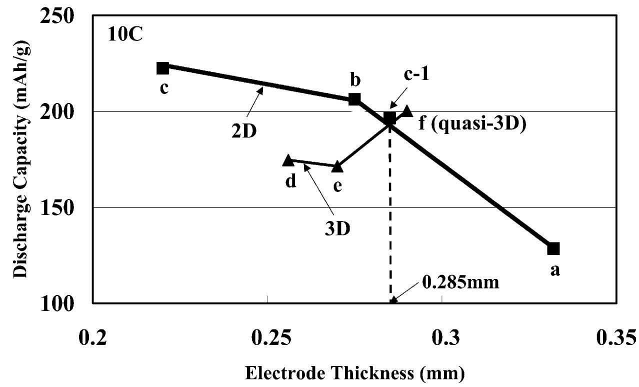

Fig. 6. Discharge capacity of the electrodes with 2D, 3D and quasi-3D substrates at 10*C* rate as a function of electrode thickness (25 °C): (a and b) punching metal (2D); (c and c-1) Ni sheet (2D); (d and e) foamed nickel (3D); (f) new developed substrate (quasi-3D).

Fig. 6 shows the summary of the electrode thickness effect on the discharge capacity at 10*C* rate of all the electrodes with the punching metal, the foamed nickel and the new developed substrates. It can be found that when the electrode thickness was less than 0.285 mm, the electrodes with the 2D substrates showed higher discharge capacity than those with the 3D ones. The discharge capacity of the electrode with the substrate e (0.270 mm) was 171 mAh/g, while that with the substrate b (0.275 mm) was 206 mAh/g. It indicated that the electrodes with the 2D substrates had better rate capability than those with the 3D substrates under the condition of the similar electrode thickness for thin electrodes. It can be also found that the discharge capacity at 10*C* rate of the electrodes with the substrates f (quasi-3D) and c-1 (2D) was almost the same. It was 200 mAh/g (f) and 197 mAh/g (c-1). The electrode thickness was 0.290 mm (f) and 0.285 mm (c-1), while the packing density for the elec-

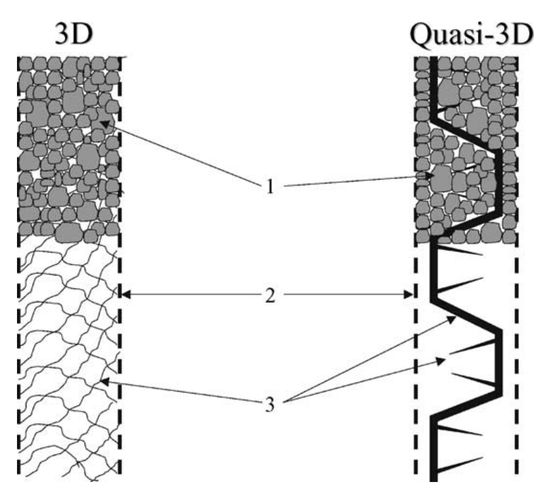

Fig. 7. Illustration of the cross-section of the electrodes with 3D and quasi-3D substrates: (1) alloy or Ni particle; (2) one side of MH electrode; (3) framework of substrate.

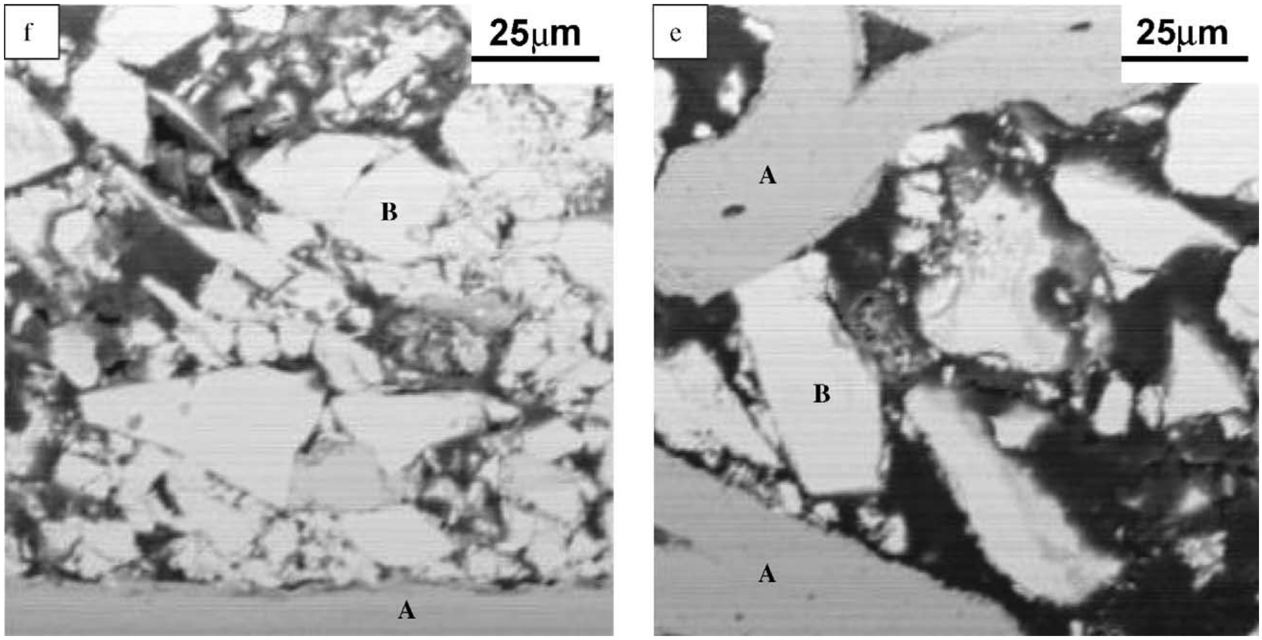

Fig. 8. SEM images of the alloy electrodes with 3D (e) and quasi-3D (f) substrates: (e) foamed nickel (3D), 0.270 mm, 28.9%; (f) new developed substrate (quasi-3D), 0.290 mm, 23.6%; (A) substrates; (B) alloys.

trode with the substrate f (5.33 g/cm^3) was slightly higher than that with the substrate c-1 (5.04 g/cm^3), respectively. It implied that compared with the electrodes with the 2D (punching metal) and the 3D (foamed nickel) substrates the electrode with the new developed quasi-3D substrate could simultaneously keep higher packing density and rate capability.

According to our knowledge, the electrodes with foamed nickel should have better conductivity between the alloy powders and the substrates due to 3D structure and larger specific surface area. However, in our work, the results showed that the electrodes with the punching metal substrates had better rate capability than those with the foamed nickel ones, mainly owning to the low electrode thickness, especially when it was lower than 0.285 mm as shown in Fig. 6. In addition, the electrode with the developed substrate f (quasi-3D) had better rate capability than those with the foamed nickel substrates (d and e). Fig. 7 shows the illustration of the cross-section of the electrodes with 3D and quasi-3D substrates, where 1 represents alloy or Ni particle, 2 represents one side of the MH electrode and 3 represents the framework of the substrate, respectively. In the quasi-3D substrate new pores were designed. However, the average pore size in substrate f was only slightly larger than that in d and e as shown in Fig. 1. It was believed that the compaction between active material (MH) and substrate framework in quasi-3D substrate would be better than that in 3D ones as shown in Fig. 8, where the electrode with the quasi-3D substrate (f) seemed compacter than that with the 3D one (e) under the condition of the similar thickness.

4. Conclusions

A new substrate (quasi-3D) combined with both 2D and 3D networks was developed. The substrate effect on the loading properties and the rate capability of MH electrodes has been investigated and compared with the conventional punching metal (2D) and foamed nickel (3D) substrates:

(1) 2D substrates (e.g. punching metal):

The α value ($=W_s$ (substrate weight)/W_e (electrode weight)) had little effect on the loading capacity. The packing density had a more important effect on the loading capacity, while the electrode thickness had a more important effect on the rate capability, while α and porosity or packing density had little effect on it.

(2) 3D substrates (e.g. foamed nickel):

The α value had a negative effect on the loading capacity based on electrode weight. Packing density had a more important effect on the loading capacity based on electrode volume than the electrode thickness.

For thin electrodes, those with punching metal substrates had better rate capability than those with foamed nickel substrates. However, for punching metal substrates, it proved that keeping high packing density contradicted keeping high rate capability.

(3) Quasi-3D substrate:

Further results showed that the new developed substrate (quasi-3D) combined with both 3D and 2D networks was more suitable for high power applications in Ni/MH batteries than punching metal (2D) and foamed nickel (3D) substrates because it could simultaneously keep high packing density and rate capability.

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