

Electrochemical properties of Bi-Ni and Bi-Ni-Mn composite-coated electrolytic manganese dioxide

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Abstract—The Bi-Ni and Bi-Ni-Mn composite is separately coated on the surface of commercial electrolytic manganese dioxide (EMD) by using a simple chemical precipitation/oxidation method. The results of X-ray diffraction show that a structure of γ -MnO₂ is kept for all the coated EMD, but the intensity of their diffraction peaks is lower than uncoated one. Both the Bi_{0.5}-Ni_{0.5} and Bi_{0.35}-Ni_{0.35}-Mn_{0.3} composite benefits the discharge capacity and high-power performance of the EMD electrodes. On the other hand, the results of scanning electron microscopy and energy dispersive spectroscopy confirm the more uniform distribution of the Bi_{0.15}-Ni_{0.55}-Mn_{0.3} composite on the surface of EMD than the Bi_{0.5}-Ni_{0.5} one, thereby resulting in better cyclability of the electrodes. After 50 cycles at a 1C rate, the capacity retention rate of the Bi_{0.15}-Ni_{0.55}-Mn_{0.3} composite-coated electrode reaches to 80%, which is far larger than the un-coated (49%) and the Bi_{0.5}-Ni_{0.5} composite-coated (63%) one.

Keywords: Electrochemical Manganese Dioxide (EMD), Bi-Ni Composite, Bi-Ni-Mn Composite, Coating, Cyclability

INTRODUCTION

Owing to an abundance of the raw materials, low production cost, low toxicity, and excellent discharge performance under low and moderate discharge rates, manganese dioxide (MnO₂) has been widely used as the positive active material in primary batteries, especially in primary manganese dioxide-zinc (Mn-Zn) batteries. According to its preparation method, there are three types of MnO₂ used in Mn-Zn battery: natural MnO₂ (NMD), chemical MnO₂ (CMD) and electrolytic MnO₂ (EMD). NMD and CMD are usually used in neutral Mn-Zn battery with NH₄Cl or ZnCl₂ electrolyte, and they are suitable for low-current and intermittent discharge. On the other hand, EMD has higher electrochemical activity, and it is usually used in alkaline Mn-Zn battery, which is suitable for high-power and continuous discharge.

Today, although there are many other batteries, such as Li-ion battery and nickel-metal hydride battery used in portable applications, the alkaline Zn-Mn battery has still taken up the majority of the worldwide battery market, in excess of US \$10 billion per annum. But the poor rechargeability of MnO₂ limits its application in alkaline second battery. It is believed that the irreversibility between Mn (IV)/Mn (II) is related to the formation of inactive Mn₃O₄ [1,2].

For ecological and economic reasons, many researchers have focused on obtaining sufficient reversible MnO₂ by means of physical and chemical modifications to it [3-9]. It was reported that the doping of Bi₂O₃, NaBiO₃ or Ni(OH)₂ into MnO₂ could prevent the formation of Mn₃O₄, thereby improving its reversibility; at the same time, the doping of Bi element into MnO₂ could increase its discharge capacity of the second electron [5-7]. In our previous study [10], we reported that the co-doping of 5 wt% Bi and 10 wt% Ni to CMD

considerably increased its rechargeability in the alkaline electrolyte, but both the maximum discharge capacity and discharge potential of the doped CMD was still obviously lower than commercial EMD.

In this study, the Bi-Ni and Bi-Ni-Mn composite was separately coated on the surface of EMD by using a simple chemical precipitation/oxidation method, and the effects of the coating on the electrochemical properties of EMD were discussed in detail. The results showed that compared to the Bi-Ni composite coating on EMD, the Bi-Ni-Mn one was more effective in improving its cyclability.

EXPERIMENTAL

Commercial EMD provided by a Mn-Zn battery company was used here. NiSO₄·6H₂O and Bi(NO₃)₃·5H₂O (also with MnSO₄·H₂O for the Bi-Ni-Mn coating) were added to distilled water at room temperature to form a homogeneous solution. As Bi(NO₃)₃·5H₂O is insoluble in distilled water, a little nitric acid was also added into it. Then, the above solution was dropwise added into a NaOH solution with 2 g commercial EMD powder at 80 °C in stirring. The mole ratio of OH⁻ to metal ions of Mn²⁺, Ni²⁺ and Bi³⁺ was 6 : 1. After the precipitation reaction was completed, a stoichiometric amount of K₂S₂O₈ was added into the reactor and the oxidation reaction was kept for 5 h at 80 °C with stirring. The obtained black powder was washed repeatedly with distilled water for the complete removal of impurity ions such as SO₄²⁻ and NO₃⁻, and finally dried at 100 °C for use. Powder X-ray diffraction (XRD) was used to analyze the phase structure of the coated manganese dioxide. Its morphology and surface composition was tested by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

The electrochemical properties of as-prepared MnO₂ were investigated in a 'sandwich-like' simulated battery containing a 7 mol l⁻¹ KOH solution at 25 °C. A commercial cadmium electrode with a large capacity was used as the counter-electrode. The pasted positive MnO₂ electrodes were made by filling a nickel foam substrate

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with a mixture of 2 wt% polytetrafluoroethylene (PTFE) binder, 20 wt% graphite and 78 wt% MnO_2 . The pasted electrodes were then dried at 65 °C and pressed to a thickness of 0.65 mm.

The simulated batteries were discharged initially at a 0.2 C rate (63 mA g^{-1}) to a cut-off voltage 0.1 V. Afterward, the batteries were charged at a 0.2 C rate for 7 h and separately discharged at a 0.2 C, 1 C (315 mA g^{-1}) or 3 C rate (945 mA g^{-1}) to a cut-off voltage 0.1 V.

Cycle life tests of the MnO_2 electrodes were performed as follows: the simulated batteries were charged at a 1 C rate for 1.2 h, rested for 10 min, then discharged at the same rate to a cut-off voltage 0.1 V.

RESULTS AND DISCUSSION

1. The EMD Electrodes with the Bi-Ni Composite Coating

The results of our previous study showed that the increase in the doping amount of Bi into MnO_2 could improve its discharge capacity, but the excess doping would cause a short circuit in the battery during cycle [10]; therefore, the coating amount of the Bi-Ni composite was controlled to 10 wt% in this paper. Fig. 1 shows the XRD patterns of EMD before and after being coated with different Bi-Ni composite. Clearly, the raw material used in this paper is $\gamma\text{-MnO}_2$. The diffraction peaks at 2θ values of 22°, 37°, 43°, 56° and 67° correspond to 101, 220, 102, 222 and 430 crystal planes of $\gamma\text{-MnO}_2$ [11], respectively. There show no obvious diffraction peaks of bismuth or nickel compounds in the XRD patterns, and this might indicate that the Bi-Ni composite has an amorphous structure. With the increase in the doping amount of Bi, the thickness of the composite might become around few micrometers or tens of micrometers (also see the explanation below for Fig. 2), therefore resulting in an obvious decrease in the intensity of the diffraction peaks.

To determine the composition of the Bi-Ni composite, the Bi and Ni compounds were prepared separately in the way described above with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (or $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) and NaOH as the raw materials and $\text{K}_2\text{S}_2\text{O}_8$ as the oxidant. The diffraction peaks in Fig. 2 confirm that in the experimental conditions, the Bi compound obtained is Bi_2O_3 (JCPDS 65-2366) and the Ni compound is NiOOH (JCPDS 06-0141); Bi_2O_3 could hardly be oxidized to NaBiO_3 in the alka-

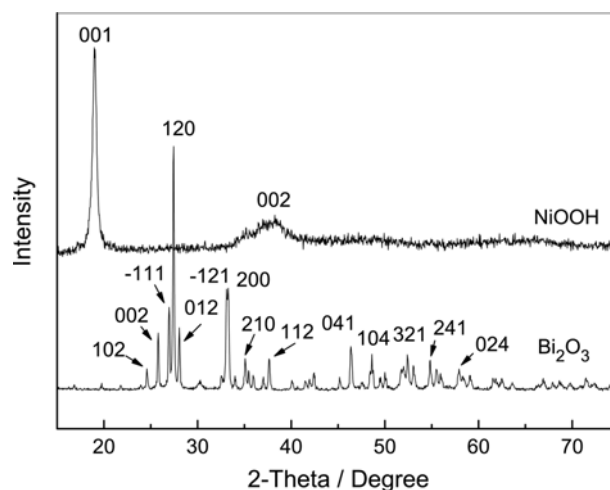


Fig. 2. XRD patterns of separately-prepared Bi_2O_3 and NiOOH .

line electrolyte by $\text{K}_2\text{S}_2\text{O}_8$. Thus, the composition of the Bi-Ni composite should be $\text{Bi}_2\text{O}_3\text{-NiOOH}$. At the same time, as shown in Fig. 2, both the separately-prepared Bi_2O_3 and NiOOH has a good crystalline structure, but as shown in Fig. 1, the co-deposited Bi-Ni composite seems to be amorphous; this might be due to the interaction between Bi and Ni in the composite. In addition, the synthesized Bi_2O_3 particles should be quite large (few micrometers or tens of micrometers) as the half-peak width (W1/2) of their diffraction peaks is quite narrow, but the intensity of the peaks is not quite strong. This might mean that the large Bi_2O_3 particles are composed of agglomerated small primary particles, and they should have high resistance and be disadvantageous to the discharge of the EMD electrode.

Fig. 3 shows the first 0.2 C discharge curves of the EMD electrodes with different Bi-Ni composite coating. All the coated electrodes show the similar discharge capacity to the uncoated one, but their discharge polarization below 0.6 V increases gradually with the increasing doping amount of Bi. It is well known that the discharge process of MnO_2 in the alkaline electrolyte is divided into two consecutive steps:

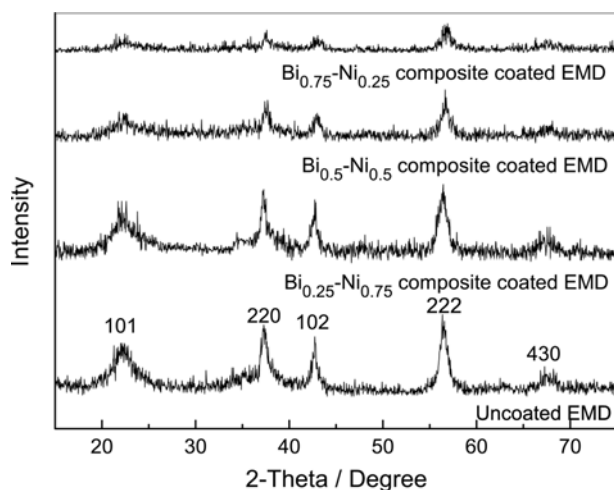


Fig. 1. XRD patterns of EMD with different Bi-Ni composite coating, where the coating amount is 10 wt%.

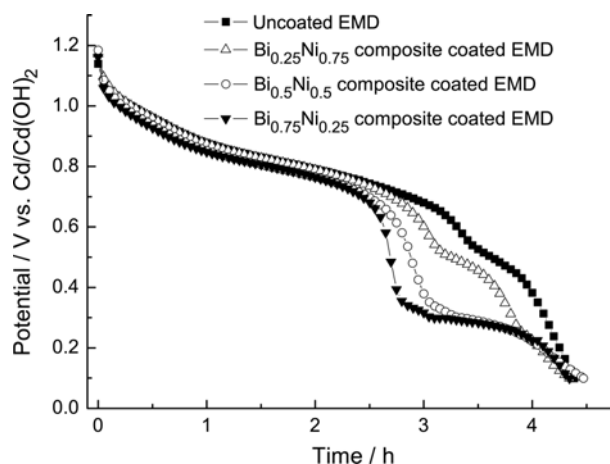


Fig. 3. 1st Discharge curves of the EMD electrodes with different Bi-Ni composite coating at a 0.2 C rate.

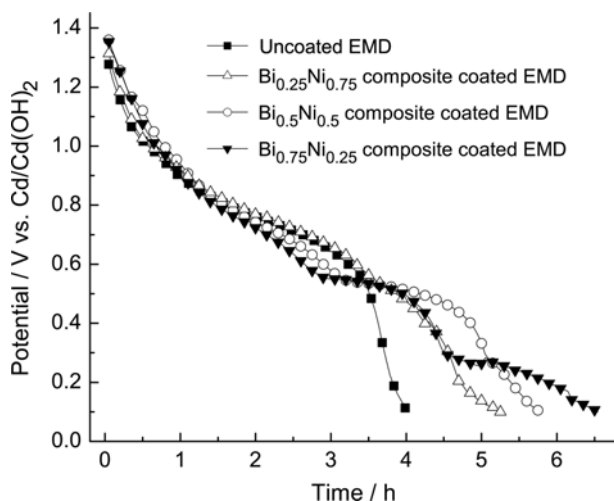


Fig. 4. 2nd Discharge curves of the EMD electrodes with different Bi-Ni composite coating at a 0.2 C rate.



The discharge potential plateaus at about 0.8 V and 0.5 V correspond to reactions (1) and (2), respectively [10]. As shown in Fig. 3, the discharge capacity of reaction (1) in the uncoated electrode is far more than reaction (2), which indicates the higher reaction polarization on the latter. The doping of Bi could benefit the reaction (2) [5,6], but the resistance of Bi_2O_3 on the surface of EMD should be greater than MnO_2 and NiOOH , and therefore, both the discharge capacity of reactions (1) and (2) in the coated electrodes decreases gradually with the increasing doping amount of Bi. The discharge potential plateau at about 0.3 V corresponds to the reduction of Bi (III) to Bi (0) [10]; this plateau is especially obvious in the $\text{Bi}_{0.75}\text{-Ni}_{0.25}$ composite-coated electrode and has little value in use because of its low discharge potential.

Fig. 4 shows the second 0.2 C discharge curves of the EMD electrodes with the Bi-Ni composite coating. Compared to the first discharge, only the uncoated electrode shows the disappearance of the discharge potential plateau at about 0.5 V, thus resulting in a capacity loss; the formation of inactive Mn_3O_4 should be responsible for it. On the contrary, all the coated electrodes show an increase in their capacity and the increase is related to the discharge process below 0.6 V, which includes the reduction of Mn (III) to Mn (II) at about 0.5 V and Bi (III) to Bi (0) at about 0.3 V. As MnOOH is converted to Mn(OH)_2 via a liquid phase process (the formation of $[\text{Mn(OH)}_4]^-$ complex ions) during the reaction (2) [12,13], the Bi-Ni composite might be no longer fully coated on the surface of EMD, then the disadvantage of Bi_2O_3 (its high resistance) to the discharge should be mitigated. On the contrary, its benefit to the reduction of Mn (III) to Mn (II) becomes more visible; therefore, the discharge capacity of the reaction (2) in the second discharge is much larger than the first discharge. The $\text{Bi}_{0.75}\text{-Ni}_{0.25}$ composite coated electrode shows the largest capacity among the coated ones, but 30% capacity of it is due to the reduction of Bi (III) to Bi (0) with little value in use.

Fig. 5 shows high-power performance of the coated EMD electrodes. Considering both the benefit and disadvantage of Bi_2O_3 to the discharge, all the coated electrodes show the larger discharge capacity but lower discharge potential than the uncoated electrode at 1 C,

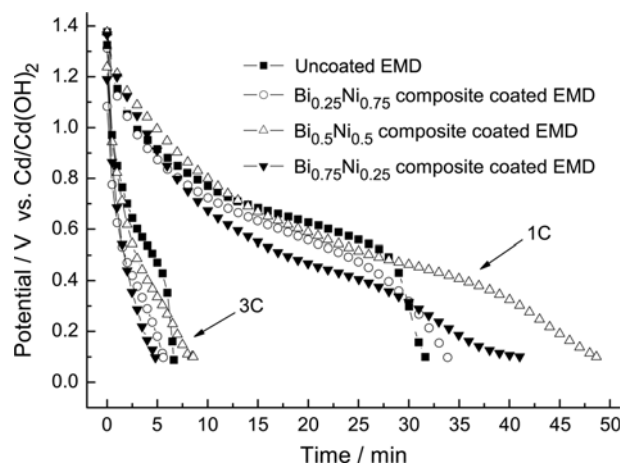


Fig. 5. Discharge curves of the EMD electrodes with different Bi-Ni composite coating at a 1 C/3 C rate.

and the $\text{Bi}_{0.75}\text{-Ni}_{0.25}$ composite-coated electrode with the largest doping amount of Bi shows the lowest discharge potential. When the discharge current increases to 3 C, the electrode's resistance becomes a significant factor to its discharge performance: only the $\text{Bi}_{0.5}\text{-Ni}_{0.5}$ composite-coated electrode shows a larger capacity than the uncoated one and the $\text{Bi}_{0.75}\text{-Ni}_{0.25}$ composite-coated electrode shows the worst discharge performance. As Bi_2O_3 benefits the discharge capacity of the MnO_2 electrode and NiOOH benefits its discharge potential [10], the $\text{Bi}_{0.5}\text{-Ni}_{0.5}$ composite-coated electrode shows the best high-power performance among the coated ones, but its discharge potential at large currents is obviously lower than the uncoated one and further improvement is needed.

Cycle life tests of the EMD electrodes with the Bi-Ni composite coating were performed and the results are shown in Fig. 6. After 50 cycles at 1 C, the capacity retention rate is 49%, 64%, 63% and 42% for the uncoated, $\text{Bi}_{0.25}\text{-Ni}_{0.75}$ composite-coated, $\text{Bi}_{0.5}\text{-Ni}_{0.5}$ composite-coated and $\text{Bi}_{0.75}\text{-Ni}_{0.25}$ composite-coated electrodes, respectively. The $\text{Bi}_{0.75}\text{-Ni}_{0.25}$ composite-coated electrode shows a slow activation during the initial cycles, since the composite might be

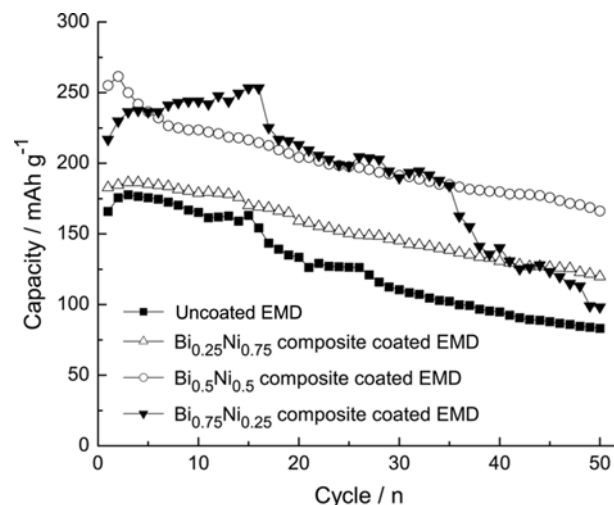


Fig. 6. Capacity of the EMD electrodes with different Bi-Ni composite coating during 50 cycles at a 1 C rate.

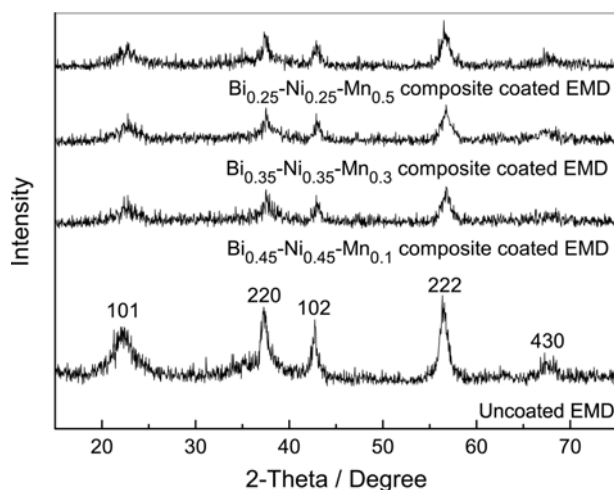


Fig. 7. XRD patterns of EMD with different Bi-Ni-Mn composite coating, where the coating amount is 10 wt%.

no longer fully coated on the surface of EMD after several cycles and the disadvantage of Bi_2O_3 to the discharge should be mitigated, but its capacity drops more quickly in the later cycles. The cyclability of the EMD electrodes can be improved effectively when the mole ratio of Ni to Bi in the composite is 1 : 1. Considering both the discharge capacity and cyclability, the $\text{Bi}_{0.5}\text{-Ni}_{0.5}$ composite coating is more suitable for the EMD electrode.

2. The EMD Electrodes with the Bi-Ni-Mn Composite Coating

Next, the mole ratio of Ni to Bi in the composite was fixed at 1 : 1, and different Bi-Ni-Mn composite was coated on the surface of EMD. Fig. 7 shows their XRD patterns. Similar to the Bi-Ni composite-coated EMD, the structure of $\gamma\text{-MnO}_2$ is kept for the Bi-Ni-Mn composite-coated one and shows no obvious diffraction peaks of other compounds in the XRD patterns; this should also indicate that the Bi-Ni-Mn composite has an amorphous structure. The intensity of the diffraction peaks also decreases obviously as the composite coated on the surface of EMD might have a thickness of few micrometers or tens of micrometers.

Fig. 8 shows the first 0.2 C discharge curves of the Bi-Ni-Mn composite-coated EMD electrodes. Similar to the Bi-Ni compos-

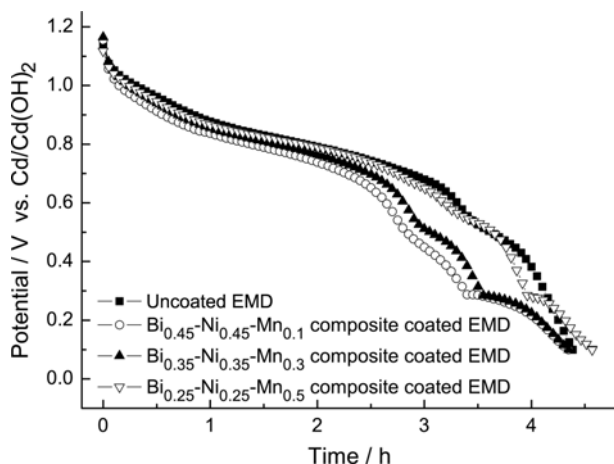


Fig. 8. 1st Discharge curves of the EMD electrodes with different Bi-Ni-Mn composite coating at a 0.2 C rate.

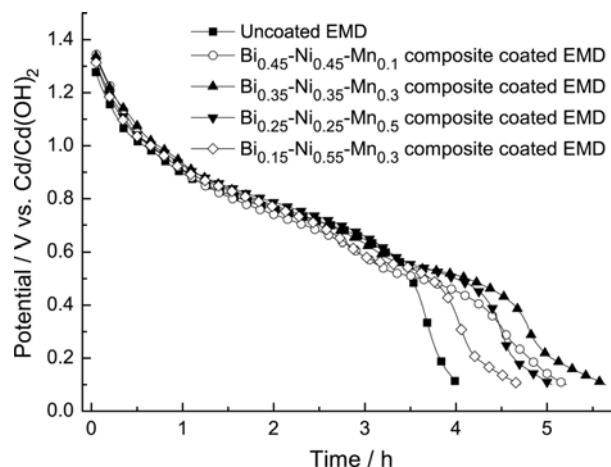


Fig. 9. 2nd Discharge curves of the EMD electrodes with different Bi-Ni-Mn composite coating at a 0.2 C rate.

ite-coated electrodes, there is indicated an obvious increase in the discharge polarization by the coating. The $\text{Bi}_{0.45}\text{-Ni}_{0.45}\text{-Mn}_{0.1}$ composite-coated electrode shows the lowest discharge potential since it has the largest doping amount of Bi. As shown in Fig. 9, during the second 0.2 C discharge, only the uncoated electrode shows the capacity fading; however, since the Bi-Ni-Mn composite might no longer be fully coated on the surface of EMD, and the doping of Bi benefits the reduction of Mn (III) to Mn (II), all the coated electrodes show an obvious increase both in the discharge capacity and discharge potential.

High-power performance of the Bi-Ni-Mn composite-coated EMD electrodes was shown in Fig. 10. Compared to the uncoated electrode, the coated electrodes show the larger discharge capacity both at 1 C and 3 C. But different from the Bi-Ni composite-coated electrodes, the Bi-Ni-Mn composite-coated ones show the similar discharge potential to the uncoated electrode at 1 C, and when the discharge current increases to 3 C, their discharge potential is only slightly lower than the uncoated electrode. This might be due to the lower resistance of the Bi-Ni-Mn composite than the Bi-Ni one.

Fig. 11 shows cycle performance of the Bi-Ni-Mn composite-coated EMD electrodes. After 50 cycles at 1C, the capacity reten-

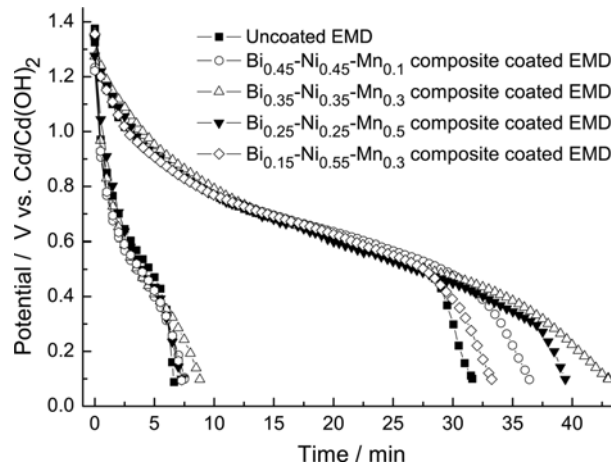


Fig. 10. Discharge curves of the EMD electrodes with different Bi-Ni-Mn composite coating at a 1 C/3 C rate.

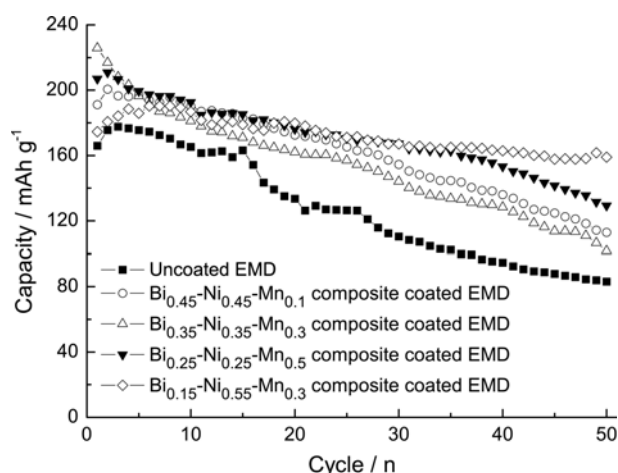
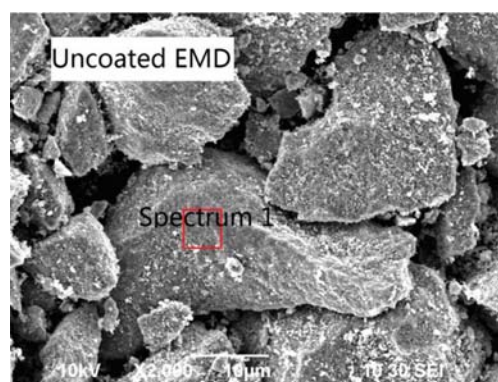


Fig. 11. Capacity of the EMD electrodes with different Bi-Ni-Mn composite coating during 50 cycles at a 1 C rate.

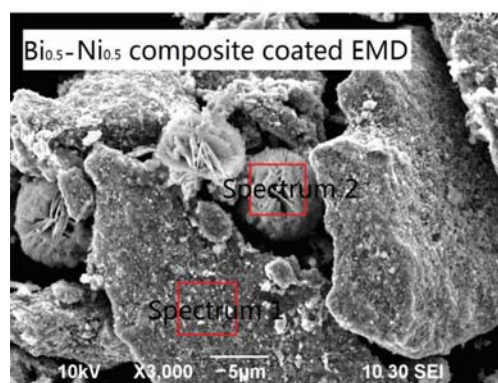
tion rate is 49%, 59%, 45% and 62% for the uncoated, $\text{Bi}_{0.45}\text{-Ni}_{0.45}\text{-Mn}_{0.1}$ composite-coated, $\text{Bi}_{0.35}\text{-Ni}_{0.35}\text{-Mn}_{0.3}$ composite-coated and $\text{Bi}_{0.25}\text{-Ni}_{0.25}\text{-Mn}_{0.5}$ composite-coated electrodes, respectively. These results seem to indicate that the cyclability of the EMD electrode increases with the increasing manganese and nickel content in the composite.

As nickel in the composite coating benefits the cyclability of the EMD electrode, and the $\text{Bi}_{0.35}\text{-Ni}_{0.35}\text{-Mn}_{0.3}$ composite coated electrode has the maximum discharge capacity among the above coated electrodes, finally, the mole content of Mn in the composite was fixed in 0.3 and the content of Ni was increased to 0.55. As shown in Figs. 9-11, although the discharge capacity of the $\text{Bi}_{0.15}\text{-Ni}_{0.55}\text{-Mn}_{0.3}$ composite-coated electrode is lower than the $\text{Bi}_{0.35}\text{-Ni}_{0.35}\text{-Mn}_{0.3}$ composite-coated one, it is still higher than the uncoated electrode. It should be particularly noticed that after 50 cycles at 1 C, the capacity retention rate of the $\text{Bi}_{0.15}\text{-Ni}_{0.55}\text{-Mn}_{0.3}$ composite-coated electrode reaches 80%, which is far larger than the uncoated and all the other coated electrodes.

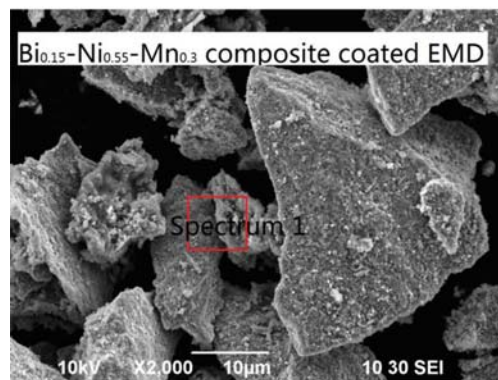
The $\text{Bi}_{0.15}\text{-Ni}_{0.55}\text{-Mn}_{0.3}$ composite has similar nickel content to the $\text{Bi}_{0.5}\text{-Ni}_{0.5}$ composite, but it improves the cyclability of the EMD electrode more effectively. To clarify the possible reason, the morphology and surface composition of the coated EMD particles was tested by using SEM and EDS, and the results are shown in Fig. 12 and



(a)



(b)



(c)

Fig. 12. SEM images of the EMD particles, where spectrum 1 and 2 are EDS mapping for them.

Table 1. Result of EDS analysis for the surface composition of the coated EMD

Element	Uncoated EMD		$\text{Bi}_{0.5}\text{-Ni}_{0.5}$ composite coated EMD		$\text{Bi}_{0.15}\text{-Ni}_{0.55}\text{-Mn}_{0.3}$ composite coated EMD	
	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C K	1.21	2.84	1.33	3.24	1.96	4.82
O K	34.33	60.50	33.85	61.97	31.05	57.31
F K	3.21	4.76	2.72	4.19	3.45	5.37
Na K	0.45	0.55	0.30	0.39	0.14	0.18
S K	0.37	0.33				
Mn L	60.43	31.02	53.34	28.44	56.50	30.37
Ni L			1.66	0.83	2.69	1.35
Bi M			6.80	0.94	4.20	0.59
Totals	100.00	100.00	100.00	100.00	100.00	99.99

Table 2. Result of EDS analysis for the surface composition of the flower-shaped particles in the $\text{Bi}_{0.5}\text{-Ni}_{0.5}$ composite coated EMD

Element	Weight%	Atomic%
C K	1.44	5.83
O K	18.74	56.86
F K	1.56	3.99
Na K	0.18	0.39
Mn L	19.11	16.88
Ni L	3.96	3.28
Bi M	55.00	12.77
Totals	100.00	100.00

Table 1. Clearly, the results of the EDS analysis confirm the deposition of the $\text{Bi}_{0.5}\text{-Ni}_{0.5}$ and $\text{Bi}_{0.15}\text{-Ni}_{0.55}\text{-Mn}_{0.3}$ composite on the surface of EMD. But different from the $\text{Bi}_{0.15}\text{-Ni}_{0.55}\text{-Mn}_{0.3}$ composite-coated EMD, there are some 'flower-shaped' particles in the $\text{Bi}_{0.5}\text{-Ni}_{0.5}$ composite-coated one. As shown in Table 2, the content of bismuth and nickel on the surface of these flower-shaped particles is far more than EMD. This seems to indicate that the addition of Mn into the Bi-Ni composite could cause more uniform distribution of the composite on the surface of EMD, thus resulting in the better cyclability improvement.

CONCLUSIONS

(1) The Bi-Ni and Bi-Ni-Mn composite was separately coated on the surface of EMD by using a simple chemical precipitation/oxidation method. The results of XRD show that the structure of $\gamma\text{-MnO}_2$ is kept for all the coated EMD, but the intensity of their diffraction peaks is lower than the uncoated one, and shows no visible diffraction peaks of bismuth or nickel compounds in the XRD patterns.

(2) Among the Bi-Ni composite coated EMD electrodes, the $\text{Bi}_{0.5}\text{-Ni}_{0.5}$ composite-coated one shows the best discharge capacity, high-power performance and cyclability. Among the Bi-Ni-Mn composite-coated EMD electrodes, the $\text{Bi}_{0.35}\text{-Ni}_{0.35}\text{-Mn}_{0.3}$ composite-coated one shows the best discharge capacity and high-power performance but the worst cyclability. On the contrary, the $\text{Bi}_{0.15}\text{-Ni}_{0.55}\text{-Mn}_{0.3}$ composite-coated electrode has discharge properties to the uncoated electrode, but after 50 cycles at 1 C, its capacity retention rate increases

by 31% than the latter.

(3) The results of the SEM and EDS analysis confirm the deposition of the $\text{Bi}_{0.5}\text{-Ni}_{0.5}$ and $\text{Bi}_{0.15}\text{-Ni}_{0.55}\text{-Mn}_{0.3}$ composite on the surface of EMD, but there appear some flower-shaped particles with particularly high content of bismuth and nickel compounds in the former. This indicates the nonuniform distribution of the $\text{Bi}_{0.5}\text{-Ni}_{0.5}$ composite on the surface of EMD, and therefore the $\text{Bi}_{0.5}\text{-Ni}_{0.5}$ composite-coated electrode shows lower cyclability improvement than the $\text{Bi}_{0.15}\text{-Ni}_{0.55}\text{-Mn}_{0.3}$ composite-coated one.

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REFERENCES

1. D. Boden, C. J. Venuto, D. Wisler and R. B. Wylie, *J. Electrochem. Soc.*, **115**, 333 (1968).
2. J. McBreen, *Electrochim. Acta*, **20**, 221 (1975).
3. M. Ghaemi, L. Khosravi-Fard and J. Neshati, *J. Power Sources*, **141**, 340 (2005).
4. H. Adelkhani, M. Ghaemi and S. M. Jafari, *J. Power Sources*, **163**, 1091 (2007).
5. D. Im, A. Manthiram and B. Coffey, *J. Electrochem. Soc.*, **150**, A1651 (2003).
6. J. Pan, Y. Sun, P. Wan, Z. Wang and X. Liu, *Electrochim. Acta*, **51**, 3118 (2006).
7. X. Xia, C. Zhang, Z. Guo, H. K. Liu and G. Walter, *J. Power Sources*, **109**, 11 (2002).
8. V. K. Nartey, L. Binder and A. Huber, *J. Power Sources*, **87**, 205 (2000).
9. M. Minakshi, M. Blackford and M. Ionescu, *J. Alloy Compd.*, **509**, 5974 (2011).
10. X. Li, Z. Li, T. Xia, H. Dong, Y. Song and L. Wang, *J. Phys. Chem. Solids*, **73**, 1229 (2012).
11. Z. Yuan, Z. Zhang, G. Du, T. Ren and B. Su, *Chem. Phys. Lett.*, **378**, 349 (2003).
12. A. Kozawa, in *Batteries, Vol. 1, manganese dioxide*, A. V. Korde-sch Eds., Marcel Dekker, New York (1974).
13. T. N. Anderson and J. M. Derby, in *Electrochemistry in transition*, O. J. Murphy Eds., Plenum, New York (1992).