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Journal of Alloys and Compounds 330–332 (2002) 776–781

Journal of ALLOYS AND COMPOUNDS

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Effects of surface structure of fluorinated AB_2 alloys on their electrodes and battery performances

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Abstract

From our previous research of fluorination treatments on improving electrochemical properties of AB_2 alloys, it was found that the fluorination technique could effectively improve the activation property and rate discharge capabilities of AB_2 alloys. In this paper, the performance of sealed batteries using fluorinated AB_2 alloys were investigated. Compared with the sealed battery using untreated AB_2 alloys, those using fluorinated AB_2 alloys showed better activation property, longer cycle life and higher rate discharge capacity. The rate discharge capacity of the sub-C sealed battery using duplicated fluorination treated AB_2 alloys reached up to 2.3 AH at 4C (10.4A). The batteries using fluorinated AB_2 alloys sustained over 300 cycles at 0.2C rate, but its discharge capacity degraded quickly when being cycled at 1C rate. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Fluorination treatment; AB_2 alloy; Impedance; Rate capacity; Cycle life

1. Introduction

Recently widely commercialized hydrogen storage alloys for power MH batteries are AB_5 type alloys. Their capacities were about 300 mAh/g. Sakai et al. have constructed cylindrical sub-C sealed batteries having a capacity of 2.83AH and a rate capacity of 2.44AH when discharged at 10A [1]. AB_2 alloys are considered to be the potential candidates due to their higher capacity around 400 mAH/g. However their activation properties, kinetic properties and cycle life could not compete with AB_5 alloys [2–6]. To overcome the poor activation property and slow kinetic properties of AB_2 alloys in electrochemical reaction, many researchers have tried various methods to modify alloy surfaces. It was reported that hot alkaline solution treatment [4] and oxidation treatment [3,7] effectively improved electrochemical performances of AB_2 alloys. Sakai and others have proposed a surface modification technique to treat hydrogen storage alloys by the chemical plating [8,9]. All the surface modification methods were to remove surface oxides and increase the catalytic Ni on surfaces of hydrogen storage alloys. Recently, a series of fluorination treatment techniques have been developed in this laboratory to modify the AB_2 alloy surface. Some research results have been summarized in some publications [10,11].

In our previous research [11,12], it was found that the metallic Ni could be deposited to AB_2 alloy surfaces through fluorination treatments. The formed Ni surface layer effectively improved electrode properties of AB_2 alloys. For example, when the alloy was treated by wet ball milling with NiF_2 and HF–KF solution through a planetary ball mill at room temperature, its activation property and the high-rate discharge capacity were found to be satisfactory compared with the conventional AB_5-based electrodes. The fluorinated AB_2 electrode demonstrated a significantly decrease of the reaction resistance. The fluorination treated alloy was found to give a large specific surface area and to form a highly Ni covered surface layer [12].

Fluorination treatments have been proved to be effective on improving the electrode properties of AB_2 alloys, but no battery data about fluorination treatment effects are available right now. It is known that the experimental conditions for testing electrode properties are different from those for testing sealed battery performances such as the amount of the electrolyte. The hydride electrodes in sealed batteries work under much more severe conditions compared with those in open cells that are widely used in electrode test. It is necessary to evaluate the surface

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PII: S0925-8388(01)01470-0

treatment effects of AB_2 alloys on their battery performances. In this paper, we investigated the effects of surface structure and specific surface area of fluorinated AB_2 alloys on sealed battery performances, and confirmed that the electrolyte consumption was the main reason to cause capacity degradation when the batteries were cycled at 1C charge–discharge rate.

2. Experimental details

2.1. Alloy preparation, fluorination treatment and testing

A typical AB_2-type alloy with C15 structure, $Zr_{0.9}Ti_{0.1}V_{0.2}Mn_{0.6}Co_{0.1}Ni_{1.1}$ has been chosen as the tested sample. The alloy preparation and fluorination treatment procedures (F-3, F-5 and F-9 treatment) have been described in our previous publication [11,12]. In order to further increase the Ni content on alloy surfaces, alloy powders after wet ball milling were then heated to 70°C for 30 min with the treatment solution. This treatment technique was named as duplicated F9 treatment. The fluorination treatment conditions are illustrated in Table 1.

Electrodes for electrode testing were made by mixing alloy powders with PTFE powders in a weight ratio of 20:1. The electrodes were packed by Ni-grid of 100 mesh then pressed into pellets with diameter of 13 mm and thickness of 1.5 mm under a mechanical load of 4 ton/cm^2. The electrodes were cycled by charging at a current of 34 mA/g for 13 h then discharging at a current of 68 mA/g to cut-off potential of −0.6 V vs. Hg/HgO electrode in 6 N KOH after resting 10 min at 20°C. The discharge capacity and electrochemical impedance spectrum (EIS) of AB_2 electrodes were measured after 15 charge–discharge cycles.

2.2. Battery assembling and testing

Positive limited cylindrical sub-C sealed batteries were assembled using pasted negative and positive electrodes. The pastes for negative electrodes were made up with alloy powders, 15 wt.% of Ni powder (Inco. 210) and 2 wt.% MC (methyl cellulose) aqueous solution. Commercialized $Ni(OH)_2$ was used as the positive electrode material after being treated by ball-milling with CoO and Co (about 3 μm) powders. A 30 wt.% KOH–10 wt.% LiOH aqueous solution was used as the electrolyte. The separator was PP (polypropylene), non-woven paper after the water-affinity treatment. The cells were sealed after being open activated by cycling 20 cycles at 0.2C charge to over charge rate of 150% and 0.2C discharge to 0.9 V vs. cell voltage. Sealed batteries contained around 4 ml of the electrolyte. The sealed battery life was tested at a 0.2C or 1C charge–discharge rate. The discharge cut-off voltage was 0.9 V.

The rate discharge capabilities were measured after 50 cycles at 0.2C charge and discharge rate. The batteries were charged at 0.2C for 6.5 h then discharged at 4C, 3.5C, 3C, 2.5C, 2C, 1.5C, 1C, 0.5C and 0.2C rate in order

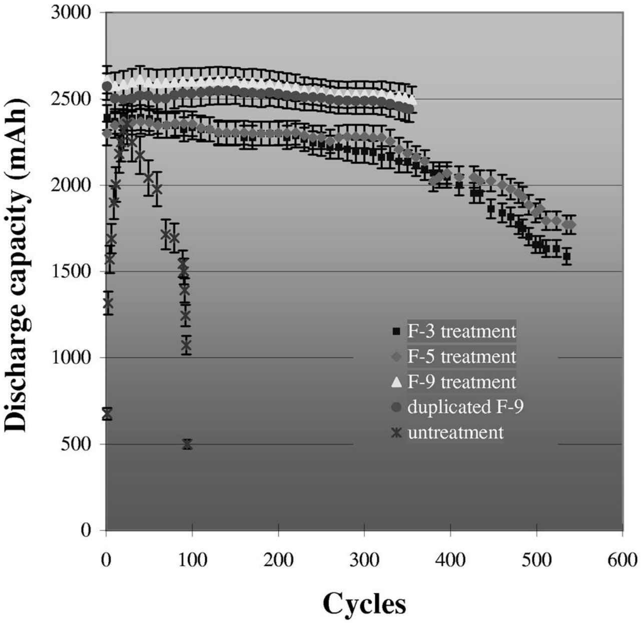


Fig. 1. Cycle behavior of sealed batteries using fluorinated AB_2 alloys at 0.2C charge–discharge rate. Charge current: 0.2C, overcharge: 120%; Rest time: 30 min; Discharge current: 0.2C to 0.9 V cut-off voltage. C=2.6AH for batteries using F-9 and duplicated F-9 treated alloy; C=2.3AH for batteries using F-3, F-5 treated and untreated alloy.

Table 1
Fluorination treatment conditions of the Zr-based AB_2 alloy

	$NaH_2PO_2 \cdot H_2O$ (g)	$Na_3C_6H_5O_7 \cdot 2H_2O$ (g)	$NiF_2 \cdot 4H_2O$	F-solution (ml)	Alloy (g)	Treatment temp. (°C)	Treatment time (min)	Ball milling speed (rpm)
F-3	2	0.25	0.4	100	5	70	30	–
F-5	0	0	0.4	100	5	70	30	–
F-9	0	0	2.4	40	10	25	90	2750
Duplicated	0	0	2.4	40	10	25(BM)	90(BM)	2750
F-9						70	30	

BM, ball milling. F-solution is composed by KF and HF aqueous solution that 1 l of treatment solution contains 6 g KF and 0.6 m1 of 48% HF fluorhydric acid.

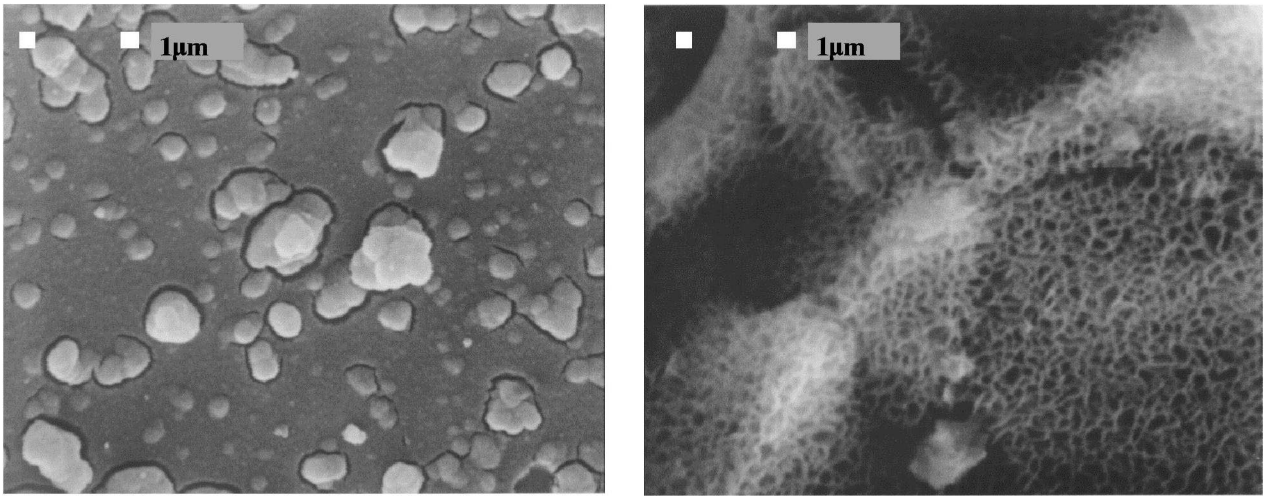
of precedence. There was a 30 min rest interval when changing discharge rates. Because the measurement conditions of the rate discharge capacity was different from those of cycling test, the discharge capacity value obtained from rate discharge capacity was usually higher than that obtained from cycling test.

3. Results and discussion

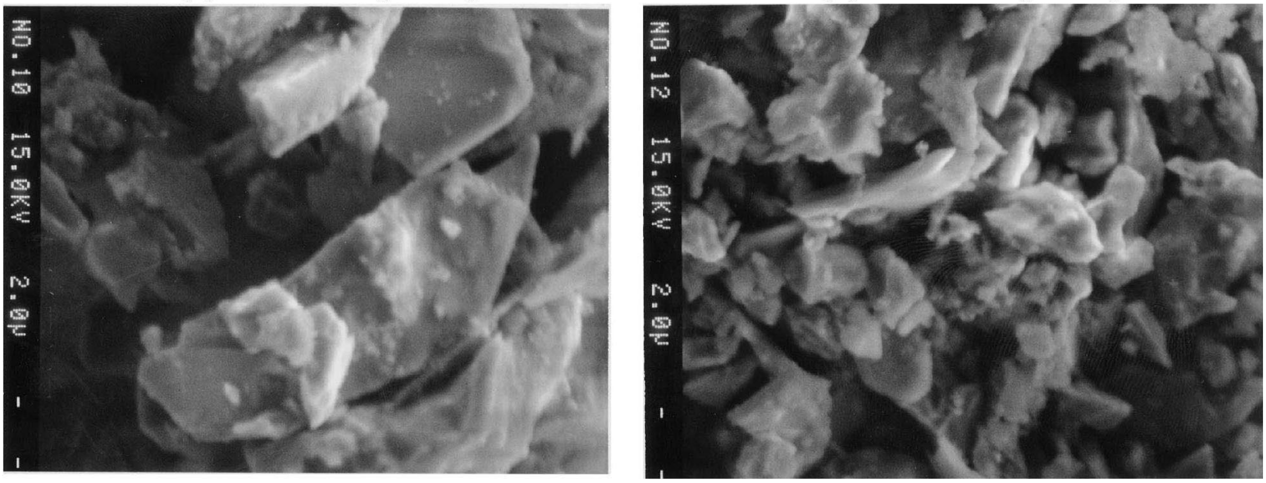
3.1. Cycle behavior of the sealed batteries

The capacity degradation of sealed batteries using fluorination treated AB_2 alloys at 0.2C charge–discharge rate is illustrated in Fig. 1. Compared with the sealed battery using the untreated AB_2 alloy, those using fluorinated AB_2 alloys showed better activation properties and longer cycle life at 0.2C. It is known that the alloy surface structure and specific surface area significantly influence the electrode properties. Fig. 2 shows the specific surface area and the surface morphology of fluorinated AB_2 alloys. The duplicated F-9 treated AB_2 alloy gave a specific surface area of 5.89 m^2/g which is 25 times as large as the untreated alloy's 0.23 m^2/g [11]. On the other hand, the XPS results showed that the untreated AB_2 alloy was covered with Zr and Mn oxides and there was no Ni existing on the top surface layer as shown in Fig. 3a. After fluorination treatment Zr and Mn oxides were eliminated and Ni was deposited to alloy surfaces. Because the Ni chemical reduction took place in the aqueous treatment solution, Ni on the top surface of the alloy existed as $Ni(OH)_2$ state as shown in Fig. 3b and c. $Ni(OH)_2$ could be converted to metallic Ni during the battery charge.

Comparing the battery using the F-3 treated AB_2 alloy



(a)F-3 treated [ref.11] (b)F-5 treated [ref.11]



(c)F-9 treated (d)duplicated F-9 treated

Fig. 2. The surface structures of fluorinated AB_2 alloy surfaces. F-3 treatment: specific surface area: 0.25 m^2/g; Maximum discharge capacity: 322 mAh/g. F-5 treatment: specific surface area: 1.82 m^2/g; Maximum discharge capacity: 360 mAh/g. F-9 treatment: specific surface area: 4.61 m^2/g; Maximum discharge capacity: 340 mAh/g. Duplicated F-9 treatment: specific surface area: 5.89 m^2/g; Maximum discharge capacity: 330 mAh/g.

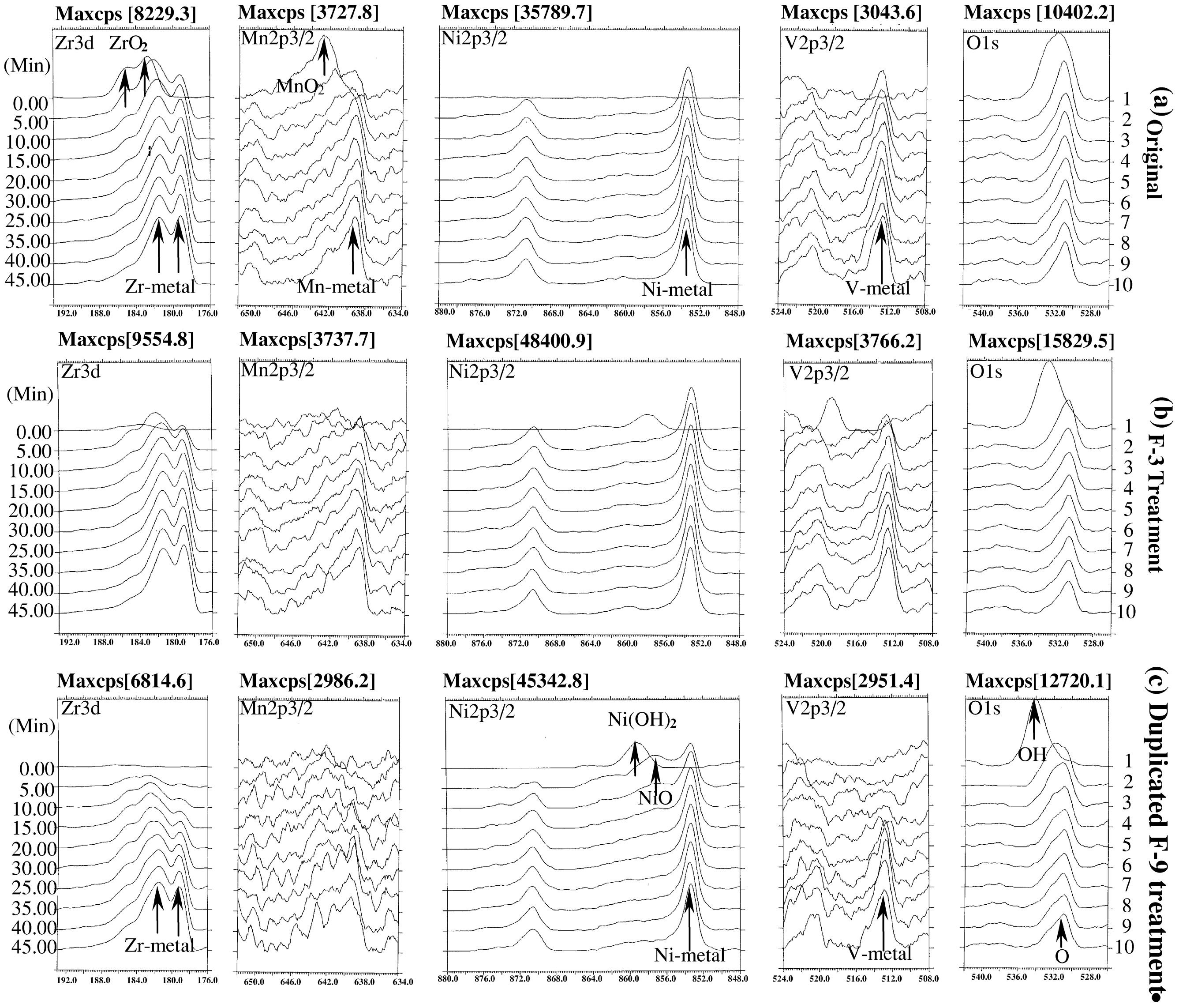


Fig. 3. XPS sputtering depth profiles of fluorinated AB_2 alloys.

with that using the untreated alloy (they had almost the same specific surface area), it was found that the activation property and cycle life of sealed batteries were improved. It was believed that the oxide removal from alloy surfaces and the creation of the metallic Ni layer on alloy surfaces improved the activation property and the cycle life because oxide surface layer was a barrier to electrochemical reaction and metallic Ni was a catalyst for the reaction. When the fluorination treatment combined with ball milling treatment (F-9 and duplicated F-9 treatment), the specific surface area of the alloy was further increased comparing with F-3 and F-5 treatment. It led to further increase the discharge capability of the sealed batteries due to the large specific surface area.

Fig. 4 shows the capacity degradation of sealed batteries using fluorination treated AB_2 alloys at 1C charge–discharge rate. Unlike being cycled at 0.2C charge–discharge rate, sealed batteries showed a sudden capacity degradation around 300 cycles when being cycled at 1C rate. After being changed to open cell (refilling the electrolyte into batteries), batteries were recovered. It was believed that this quick capacity degradation was caused by the electrolyte consumption when the batteries being cycled at 1C, which agreed with the conclusion Knosp et al. have made [13]. It has been pointed out that the corrosion rate of AB_2 alloys was nearly equivalent to that of AB_5 alloys, but corrosion consequences on the water consumption and negative discharge reverse were more severe for AB_2 alloys. In order to further improve the cycle life of the batteries using AB_2 alloys, how to decrease the electrolyte consumption would be the key point. It is necessary to further lower the corrosion rate of AB_2 alloy and improve

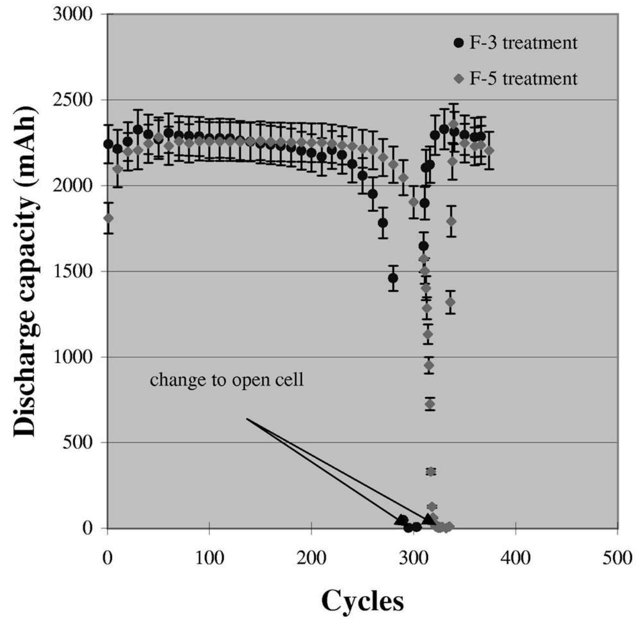
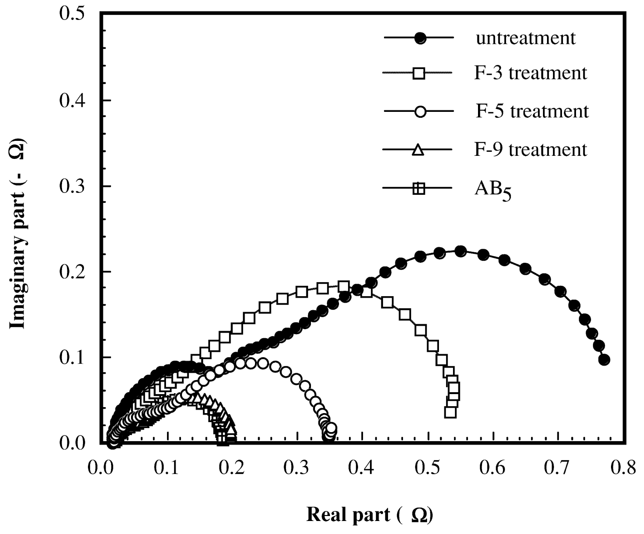


Fig. 4. Cycle behavior of sealed batteries using fluorinated AB_2 alloys at 1C charge–discharge rate. Charge current: 1C, overcharge: 120%; Rest time: 30 min; Discharge current: 1C to 0.9 V cut-off voltage. C=2.3AH.



AB_2 alloy: $Zr_{0.9}Ti_{0.1}V_{0.2}Mn_{0.6}Co_{0.1}Ni_{1.1}$
AB_5 alloy: $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$
DOD: 50%
Temperature: 20•

Fig. 6. Electrochemical impedance spectrum of fluorinated AB_2 alloys.

the gas recombination capability of the negative electrode in the sealed battery.

3.2. Rate discharge capability

Fig. 5 shows the rate discharge capabilities of the batteries using fluorination treated AB_2 alloys. The batteries using fluorination treated alloys showed higher rate capacities than that using the untreated alloy. The batteries using fluorination treated alloys with a larger specific surface area demonstrated a higher rate discharge capability. It was found that the rate discharge capacity of the battery using duplicated fluorination treated AB_2 alloys reached up to 2.3 AH at 4C (10.4A) which was close to 2.44AH when discharge at 10A for the battery using treated AB_5 alloy [1].

The EIS measurement results showed that the reaction impedance decreased when specific surface area of fluorinated alloys increased as shown in Fig. 6. Compared to the untreated AB_2 alloy, fluorinated AB_2 alloys showed rather lower reaction impedances. It can be attributed to the surface oxide elimination, large specific surface area and the formation of metallic Ni surface layer that works as catalytic sites for charge and discharge. Correspondent rate discharge capabilities of the batteries using fluorinated alloys (Fig. 5) to their reaction impedances (Fig. 6), it was found that the sealed batteries using fluorinated alloys with a lower reaction impedance demonstrated a higher rate discharge capacity.

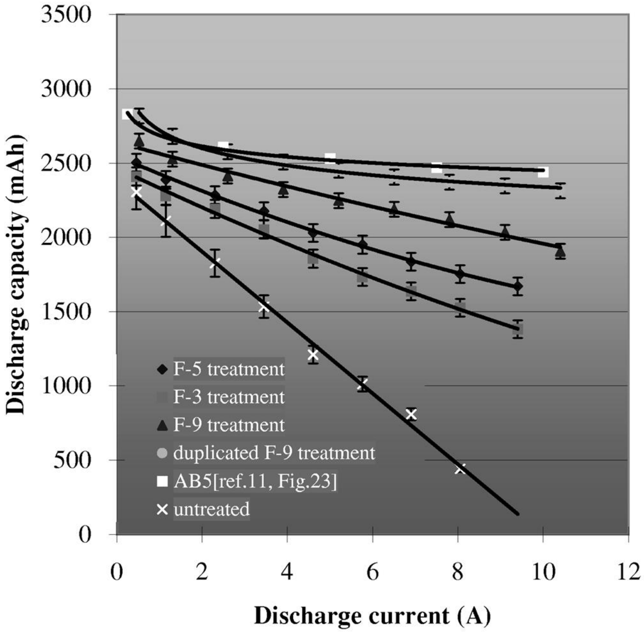


Fig. 5. Rate discharge capabilities of sub-C sealed batteries using fluorinated AB_2 alloys.

4. Conclusions

Cylindrical sub-C sealed batteries using fluorinated AB_2 alloys demonstrated a discharge capacity of 2.6 AH. They showed higher rate capacities, better activation properties and longer cycle life at 0.2C charge–discharge rate compared with that using untreated AB_2 alloy. However the batteries showed a sudden decrease in discharge capacity when being cycled at 1C charge–discharge rate due to the electrolyte consumption. In order to improve the cycle life of sealed batteries using AB_2 alloys, further efforts are needed to decrease the electrolyte consumption during cycling at a higher charge–discharge rate.

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