Electrochemical investigation on hydride electrode with tungsten carbide additive[①]

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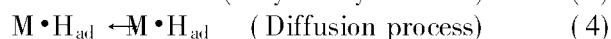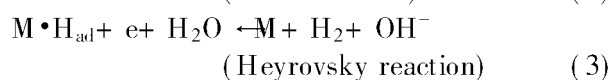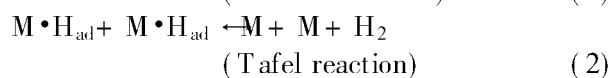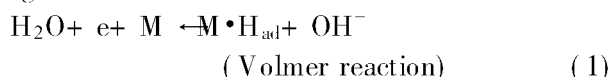Hangzhou 310014, P. R. China

Abstract: Nano-meter-sized WC powder (1~ 20 nm) was synthesized by mechanochemical explosion synthesis. The catalytic property of WC powder was discovered to decompose the molecular water and chemical-adsorb H atoms in KOH solution, and accelerate the combination reaction of hydrogen during the cathodic polarization, thus a negative effect on the activation was found because of easy H_2 emission. Electrochemical impedance spectroscopy (EIS) showed that the ad-sorbed hydrogen atoms on the surface of WC are first electrochemically oxidized due to their lower chemical bonding, and that the low conductivity of WC powder also increases the internal resistance of electrodes.

Key words: hydrogen storage alloys; tungsten carbide; electrode performances; EIS　　　　　**Document code: A**

1 INTRODUCTION

Generally, in the charge (cathodic) process of hydrogen storage alloy electrodes, the electrolysis of water takes place and the atomic hydrogen first ad-sorbs on the surface of electrode according to reaction (1) at the potential of − 0. 828 V vs Hg/ HgO. As the cathodic potential (absolute value) increases and the coverage of hydrogen adsorbed on surface rises, then hydrogen gas bubbles through the combination reaction (2) or reaction (3)[1]. The adsorbed hydro-gen atoms can also penetrate simultaneously into the bulk of alloy by reaction (4), accompanying the par-tial ionization of hydrogen atom with the electron transfer from metal atoms. When the hydride elec-trodes are discharged, transfer of hydrogen from the absorbed sites in the surface sublayer to the adsorbed sites on the surface will set in according to reaction (4), then the electrochemical oxidation of adsorbed hydrogen atoms concurs.

$$H_2O+ e+ M \rightleftharpoons M \cdot H_{ad}+ OH^-$$
$$(Volmer\ reaction) \qquad (1)$$
$$M \cdot H_{ad}+ M \cdot H_{ad} \rightleftharpoons M+ M+ H_2$$
$$(Tafel\ reaction) \qquad (2)$$
$$M \cdot H_{ad}+ e+ H_2O \rightleftharpoons M+ H_2+ OH^-$$
$$(Heyrovsky\ reaction) \qquad (3)$$
$$M \cdot H_{ad} \rightleftharpoons M \cdot H_{ad} \qquad (Diffusion\ process) \qquad (4)$$

The charge/ discharge process could be affected by some additives in hydride electrodes such as RuO_2, Co_3O_4, CoO, La_2O_3, MnO_2, NiO and Al_2O_3[2] and Bi_2O_3[3], or in the electrolytes such as KBr[4], KBH_4[5] and ZnO[6]. There are indications that tran-sition metal carbides have many of the desirable catalytic properties similar to the noble metals (Pd and Pt) with respect to hydrogen oxidation and hy-drogenolysis reactions[7, 8]. The nano-structure would provide an ultrahigh specific surface area and exhibit outstanding catalytic properties as well. In this pa-per, an attempt is made to understand the role of nano-meter-sized WC powder additive on the electro-chemical performances of a metal hydride electrode. The host hydrogen storage alloy $Zr_{0.5}Ti_{0.5}(Mn_{0.25}V_{0.15}Ni_{0.55})_2$ was chosen because this alloy has promising electrochemical properties and could act as a candidate for commercializing electrode materials. Meanwhile, we also try to discuss the electrocatalytic activity of WC powder by the tentatively electro-chemical impedance analysis.

2 EXPERIMENTAL

Nano-meter-sized WC powder was prepared from the stoichiometric mixture of WO_3, Mg and C pow-ders through mechanochemical explosion synthesis. Its nano-structure was estimated to be about 1~ 20 nm in size by high resolution electron microscope as shown in Fig. 1. Usually the ultrafine WC particle is of monocrystalline with some defects such as twins, and is encapsulated by monolayer graphite.

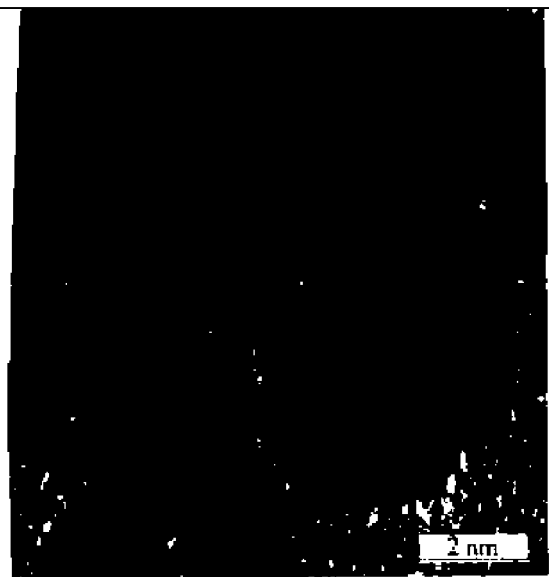The alloy $Zr_{0.5}Ti_{0.5}(Mn_{0.25}V_{0.15}Ni_{0.55})_2$ was

Fig. 1 High-resolution TEM image of
nano-meter-sized tungsten carbide powders

prepared by induction melting under 100 kPa argon atmosphere. The test electrodes were prepared by cold-pressing the mixture of hydrogen storage alloy powder (< 43 µm), WC powder and Cu powder (43 µm) in a mass ratio of 1: K: 2(K = 0, 0. 1 or 0. 2) to form porous pellets of 10 mm diameter. Electrochemical charge-discharge tests were carried out in trielectrode electrolysis cells, in which the counter-electrode was nickel hydroxide with a larger capacity, the reference electrode was Hg/HgO, and the electrolyte was 6 mol/L KOH solution. The discharge capacities of hydride electrodes were determined by galvanostatic method. Electrochemical impedance spectroscopy measurements were applied to study the surface state of electrode by using Solartron 1250 Frequency Response Analyzer in conjunction with a Solartron 1287 Electrochemical Interface. The voltage perturbation was 10 mV and the frequency region was between 6. 5 kHz and 6. 5 mHz.

3 RESULTS AND DISCUSSION

The electrochemical experiments were applied to the $Zr_{0.5}Ti_{0.5}(Mn_{0.25}V_{0.15}Ni_{0.55})_2$ hydrogen storage alloy electrodes without and with nano-meter-sized WC powder additive at 293 K. Prior to the experiments all the electrodes were submerged in 6 mol/L KOH solution for 30 min to ensure being saturated with electrolyte. Fig. 2 depicts the cathodic polarization curves on the first charge of the electrodes without/with 10% and 20% WC powder additive at a constant charge current of 100 mA/g (based on the alloy mass). It can be seen that after KOH immersion the starting potentials are − 0. 458 V (vs Hg/HgO) for WC-free electrode, − 0. 738 V for 10% WC electrode and − 0. 747 V for 20% WC electrode, respectively. The WC additives impose an apparent influ-

ence on the starting electrode potential. While the amounts of WC additive (10% and 20% WC) do not exert too much difference to the potentials. Once the charge current (100 mA/g) was applied, all three electrode potentials dropped by about 350 mV. This implies that the three electrodes have almost the same resistance 3. 5 Ω/g (polarization and contact resistances). The potentials of the electrodes with WC additive reached the constant values, i. e. − 1. 124 V for 10% WC electrode and − 1. 101 V for 20% one, where gaseous hydrogen bubbling took place. The result shows that the WC-added electrodes are covered with hydrogen atoms even when it immerses into KOH solution without any cathodic polarization. Therefore the electrode potential is determined by the chemical potential of hydrogen atoms adsorbed on the surface of WC powder. WC powder plays a role of catalyst to decompose water molecular and to build up a hydrogen adsorption layer, during this process the alloy components act as electron donator.
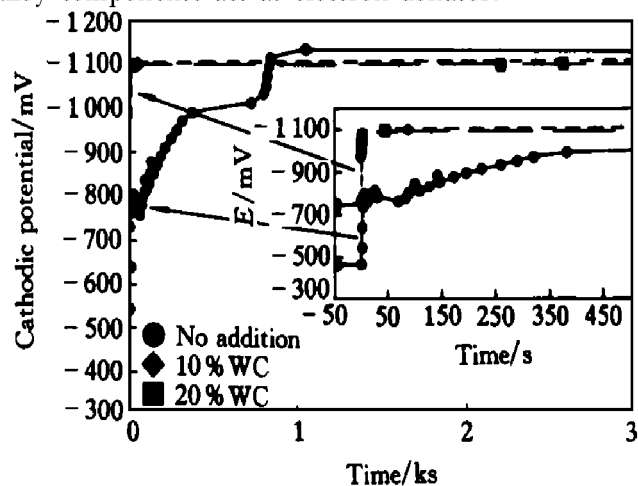

Fig. 2 Cathodic curves of $Zr_{0.5}Ti_{0.5}(Mn_{0.25}V_{0.15}Ni_{0.55})_2$ electrodes doped with WC additive,
at cathodic current of 100 mA/g and 293 K

In comparison with the E —t curves of the WC-added electrodes, the WC-free electrode has a different shape. When the cathodic current was applied, the electrode potential decreased gradually, accompanying the reduction of oxide surface of both alloy and copper powders. A potential plateau existed at about − 1. 0 V, which was attributed to the hydrogen atoms adsorbed on the surface of alloy powder. From the plateau width about 460 s the amount of adsorbed hydrogen atoms could be calculated to be about 4. 77 × 10^{-4} mol/g. Considering the alloy particle has a spherical size of 4 µm, the coverage of hydrogen is roughly 2. 38 × 10^{-7} mol/cm. As the charge time prolonged, another potential plateau followed at − 1. 2 V, where hydrogen gas evolved. It is clear that the potential of H_2 evolution is more negative for the WC-free electrode than that for WC-added ones.

Fig. 3 shows the anodic polarization curves of the electrodes at a discharge current of 50 mA/g after

their first charging for 4 h. The WC-free electrode exhibits a larger discharge capacity of 213 mAh/g compared to 110 mAh/g for the 20% WC-added electrode. The result shows that less amount of hydrogen absorbed in the bulk of alloy with the presence of WC powder, because the WC powder resulted in more hydrogen emission through the rapid combination (Tafel or Heyrovsky reaction).
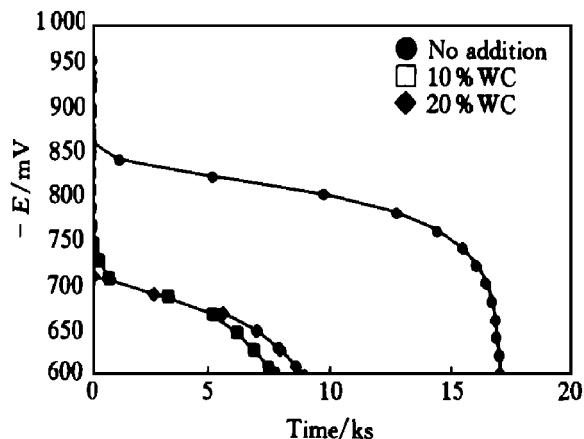

Fig. 3 Anodic curves of $Zr_{0.5}Ti_{0.5}(Mn_{0.25}V_{0.15}Ni_{0.55})_2$ electrodes doped with WC additive, at discharge current of 50 mA/g and at 293 K

Fig. 4 shows the discharge capacity vs cycle number of electrodes without and with WC additive. Initially the WC-free electrode exhibited a larger discharge capacity than the WC-added ones. However, after 3 cycles all three electrodes attained their maximum discharge capacities respectively. The effect of WC powder additive on accelerating the hydrogen combination gradually decreased as the cycle number increased. As the hydrogen storage alloy surface was activated and the hydrogen diffusion channel in the bulk of alloy set up, hydrogen combination on WC was restrained due to the rapid hydrogen absorption into alloy. This indicates the presence of WC powder additive hinders the activation of hydride electrodes in spite of its excellent catalytic property. From the above discussion we could also draw another conclusion that less active electrocatalytic hydride electrode can attain a higher electrode potential, the adsorbed hydrogen atoms with a higher chemical potential, therefore, can penetrate into the bulk of alloy more rapidly without obvious hydrogen emission. Whereas if no additive, the equilibrium potential of the charged electrode depended mainly on the inherent property of the A-side hydride forming elements[9].

Fig. 5 depicts the linear micro-polarization curves of the studied electrodes at different equilibrium potentials. In this paper, two typical equilibrium potentials were chosen: at the full charge state (being charged at 100 mA/g for 4 h) and at the discharge state (being discharged at 50 mA/g to − 0.6V). The exchange current density i_0 was calculated according to $i_0 = RTi/(F\eta)$ [10] and listed in Table 1. The elec-

trode with a richer hydrogen content exhibited a larger exchange current density, and a less reaction resistance. The WC additive can increase the exchange current density especially for the electrode in discharge state. This increase is attributed to the hydrogen adsorbed on WC powder with a mild affinity.
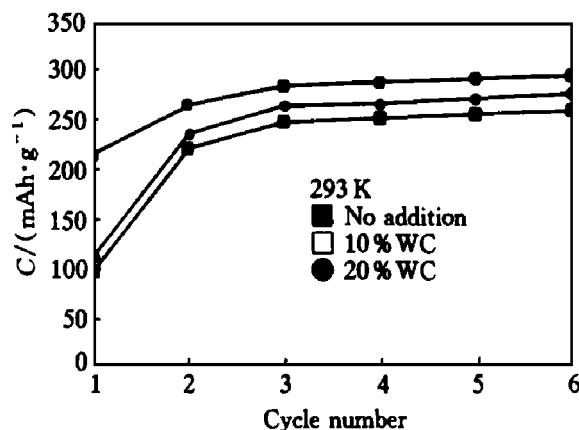

Fig. 4 Discharge capacity vs cycle number of $Zr_{0.5}Ti_{0.5}(Mn_{0.25}V_{0.15}Ni_{0.55})_2$ electrodes at charge current 100 mA/g and discharge current 50 mA/g

Table 1 Exchange current densities i_0 of $Zr_{0.5}Ti_{0.5}(Mn_{0.25}V_{0.15}Ni_{0.55})_2$ electrodes doped with WC additive at different equilibrium electrode potentials

Electrode	Charge state		Discharge state	
	E_{eq}/V	i_0/(mA·g⁻¹)	E_{eq}/V	i_0/(mA·g⁻¹)
WC-free	− 0.942 31	25.6	− 0.824 65	6.7
10% WC	− 0.928 95	30.1	− 0.846 58	10.7
20% WC	− 0.929 08	30.6	− 0.835 01	10.5

EIS analysis was performed to further elucidate the influence of WC powder on the interfacial behavior of hydride electrode. The electrodes were discharged on the second cycle to cut-off potential, and then charged at 100 mA/g for 10 min at 293 K. Fig. 6 shows the Nyquist plots of the three electrodes with relatively low hydrogen concentrations. The WC-free electrode showed a perfect semicircle representing the electrochemical reaction resistance, however, the Nyquist plots of the WC-added electrodes became more complicated. The salient changes were found in the high frequency region (in the front part of the plot) as shown in Fig. 6(b). An extra obvious semicircle appeared, and its size enlarged as the amount of WC increased. Thus extra plot could be attributed to the presence of WC additive and the hydrogen atoms adsorbed on its surface, the high coverage of hydrogen in the WC-added electrodes was reasonable. If considering our experimental process that these electrodes were charged for a short time, the WC powder was believed to be first covered by the hydrogen atoms, alternatively, the front semicircle is related to the electrochemical oxidation of hydrogen
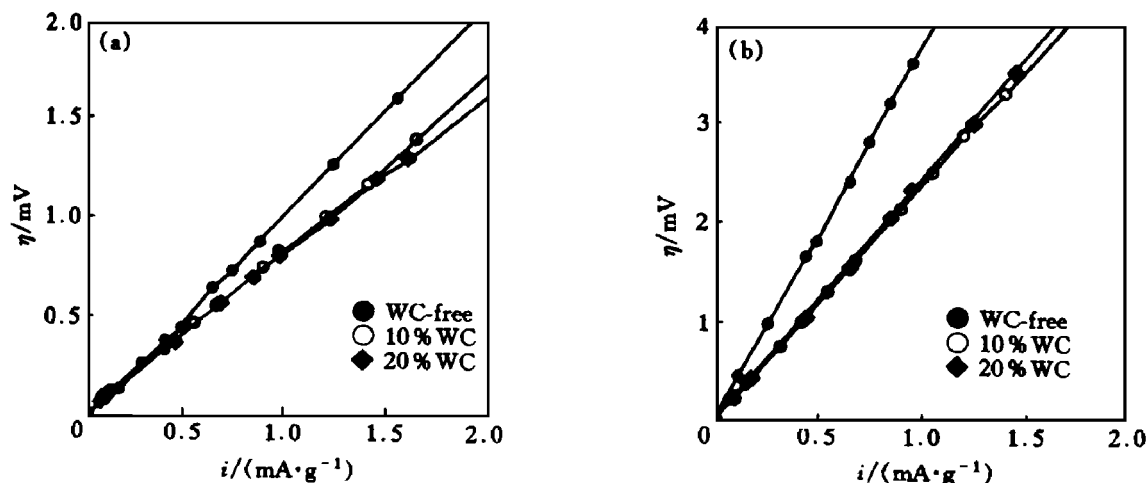
Fig. 5 Linear micro-polarization curves of $Zr_{0.5}Ti_{0.5}(Mn_{0.25}V_{0.15}Ni_{0.55})_2$ electrodes doped with WC additive at different states of charge
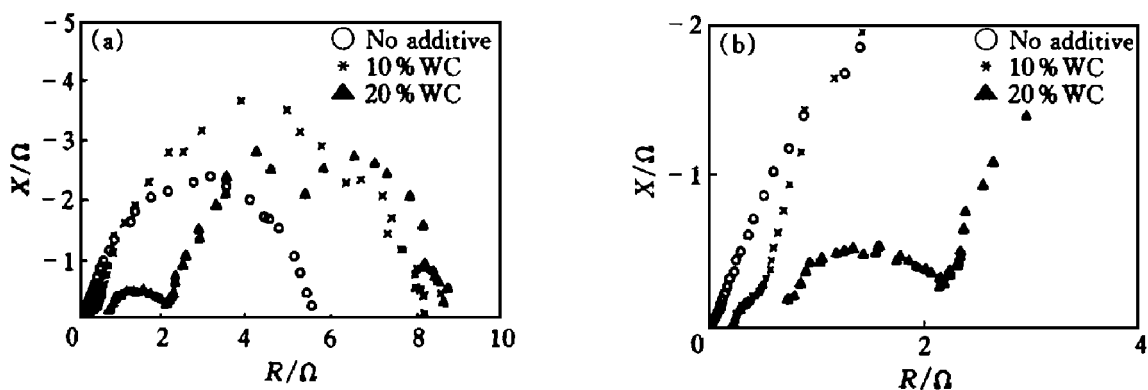(a) —Full charge state; (b) —Discharge state

Fig. 6 Impedance spectra of $Zr_{0.5}Ti_{0.5}(Mn_{0.25}V_{0.15}Ni_{0.55})_2$ electrodes doped with WC powder additive
(All electrodes are discharged to − 0. 6 V and then charged at 100 mA/ g for 10 min at 293 K)

atoms adsorbed on the WC surface. Furthermore, the WC additive also brought forth the increase in contact resistance among alloy particles as the starting point in the Nyquist plots moved to a higher resistance region. The result can also back our previous conclusion concerning the discharge kinetics. The WC powder also influenced the electrochemical reaction process, which was indicated by the irregular shape of larger semicircle in low frequency regime.

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