# Electrocatalysis induced by surface-modification with Pd through sol–gel method for $Ti_{33}V_{20}Cr_{47}$ alloy

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## ARTICLE INFO

## ABSTRACT

A body-centered-cubic (bcc) phase $Ti_{33}V_{20}Cr_{47}$ alloy surface-modified with Pd particles was prepared through sol–gel method. The composite showed significantly improved electrochemical hydrogen release capacities, reaching 225 mAh g$^{-1}$ at a discharge current of 60 mA g$^{-1}$ at 293 K in the second cycle. Such a large capacity could be attributed to the contribution of catalysis of Pd particles, which induced the $Ti_{33}V_{20}Cr_{47}$ alloy to release hydrogen more easily. These results provide a new approach to wide applications of Ti–V-based bcc phase alloys in high-energy batteries.

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## 1. Introduction

BCC type Ti–V–Cr alloys exhibit excellent effective hydrogen storage capacity of >2% (mass percent, ditto) and a proper plateau pressure in the pressure–composition (P–C) isotherm for the absorption and desorption of hydrogen, which makes them suitable as anode material in Ni–MH batteries [1–3]. However, these alloys are barely activated during charging in alkaline solution due to the formation of a dense oxide layer on their surface [4,5]. In order to induce their electrochemical activity some second phases such as TiNi phase and C14 laves phase should be introduced into the alloys [6–8], or surface-modified with LaNi$_5$ and La–Mg–Ni alloys prepared simply by ball milling [9–11]. But all these methods reduce the V-based alloy's own capacity significantly while improve performance of the electrode.

In this paper, to improve the electrode characteristics of $Ti_{33}V_{20}Cr_{47}$ alloy, the effect of surface- modification with Pd particles through sol–gel method on the capacity of hydrogen storage alloys was investigated. There was only a little loss of the hydrogen storage capacity of the alloy, however it dramatically improved the performance of electrode characteristics of Ti–Cr–V alloys. It was also shown that the Ti–Cr–V alloys could be modified in solution.

## 2. Experimental

$Ti_{33}V_{20}Cr_{47}$ alloy sample was prepared by magnetic levitation melting. To ensure the homogeneity and avoid oxidation of the alloy, a 50 g ingot was turned over and remelted four times in the ambience of argon. The as-cast ingot was crushed into powder under 200 mesh for X-ray diffraction (XRD) measurement and P–C isotherm measurement.

Colloidal palladium (Pd) was purchased from Shenzhen Tianli Plating Materials Port Co. Ltd. China. Powders of

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$Ti_{33}V_{20}Cr_{47} + 4\%$ Pd were produced by sol–gel method. The required amount of NaCl was added, stirring until complete dissolution (210 g/L). Then HCl was added (5 mL/L, the tank is topped up with water to the make-up level. Finally colloidal Pd was added (100 mg/L). All pumps and heaters were switched on and heated up to set temperature (5 min, 308 K). The $Ti_{33}V_{20}Cr_{47}$ alloy powder was added and stirred for 5 minutes. Then $H_2SO_4$ was added (20 mL/L). The mixture was filtered, washed and dried at 353 K for more than 1 h.

The crystal structure and lattice parameters of the powder were examined by X-ray diffractometer using Cu Kα radiation (Rigaku, D/Max2200/PC). The microstructures were observed by scanning electron microscopy (Hitachi S-4700).

P–C isotherm curves quantitatively characterizing the hydrogen desorption properties of hydrogen storage alloys were measured by a Sieverts-type gas reaction controller (GRC), a product of Advanced Materials Corporation (USA). Alloy powder sample of 3 g was weighed and sealed into the sample reaction chamber which was evacuated at 773 K for 3 h before P–C isotherm measurement.

The alloy powder was mixed with Ni powder in a weight ratio of 1:4, and 1.5 g of the mixture was pressed under a pressure of 300 MPa to form a circular pellet of 15.5 mm diam. Electrochemical measurements were performed in a three-electrode system with a 6 mol/L KOH aqueous solution used as electrolyte. $Ni(OH)_2$/NiOOH and Hg/HgO were used as the counter electrode and reference electrode respectively. The charge–discharge measurements were performed by an automatic galvanostatic system (DC-5) and each negative electrode was charged at 60 mA g$^{-1}$ with a potential limit of −2 V and discharged at 60 mA g$^{-1}$ with a cutoff voltage set at −0.5 V (vs. Hg/HgO).

## 3. Results and discussion

### 3.1. Effect of surface-modification on the structure of alloy powders

It is known that nanocrystalline materials possess ultrafine grains with a large amount of grain boundaries that may act as fast atomic diffusion channels. The grain boundaries with various kinds of nonequilibrium defects also constitute a high excess of energy that may further facilitate their chemical reactivity [12]. Fig. 1 shows the XRD of the $Ti_{33}V_{20}Cr_{47}$ alloy before and after surface-modification. The sample before surface-modification displays one phase: $Ti_{33}V_{20}Cr_{47}$ with bcc structure. After surface-modification, the diffraction peaks of Pd appeared while the diffraction peaks of bcc phase showed no significant change. This is the result of the Pd particles precipitated out from the colloid and deposited on the alloy surface.

Fig. 2 shows the SEM image of $Ti_{33}V_{20}Cr_{47}$ and $Ti_{33}V_{20}Cr_{47} + 4\%$Pd powder. It is suggested that the BCC type $Ti_{33}V_{20}Cr_{47}$ alloy is encapsulated by the Pd particles. The Pd particles on the BCC alloy surface may provide a short cut for absorption and desorption of hydrogen, and contribute to the improvement in the surface activation of the electrode.
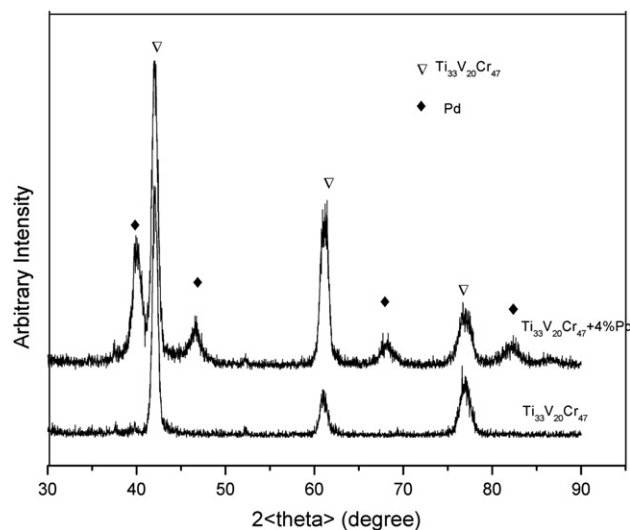


**Fig. 1 – XRD patterns of $Ti_{33}V_{20}Cr_{47}$ alloy and $Ti_{33}V_{20}Cr_{47} + 4\%$Pd alloy.**

### 3.2. Desorption behavior of hydrogen in the alloy

Fig. 3 shows hydrogen desorption curves of the $Ti_{33}V_{20}Cr_{47}$ and $Ti_{33}V_{20}Cr_{47} + 4\%$Pd alloy powder at 353 K. The $Ti_{33}V_{20}Cr_{47}$ alloy exhibits a maximum hydrogen storage capacity of approximately 3.45% $H_2$ and for $Ti_{33}V_{20}Cr_{47} + 4\%$Pd it is 3.2% $H_2$. There are two reasons why the addition of Pd decreases the hydrogen storage capacity of $Ti_{33}V_{20}Cr_{47}$ alloy. Firstly, Pd possesses lower hydrogen absorption capacity (1.8%) in comparison with $Ti_{33}V_{20}Cr_{47}$ alloy (3.45%). Another reason could be that a part of $Ti_{33}V_{20}Cr_{47}$ alloy is eroded during preparation in acid. Compared with other approaches, there is only a little decrease of the hydrogen absorption capacity of the alloy. The hydrogen desorption performance of alloys is dependent on their maximum hydrogen storage capacity and hydrogen desorption plateau pressure both [13]. As the Pd deposited on $Ti_{33}V_{20}Cr_{47}$ alloy surface, hydrogen storage capacity decreased 0.25%, while the desorption plateau pressure of the alloy increases, which induces the alloy to release hydrogen more easily. This is important in practical applications. From Fig. 3, we can see the desorption of $Ti_{33}V_{20}Cr_{47}$ alloy is 2.25% and for $Ti_{33}V_{20}Cr_{47} + 4\%$Pd it is 2.1%, there is 0.15% decrease of desorption capacity, lower than that of absorption 0.25%.

### 3.3. Effect of Pd addition on the discharge performance and cycle life of alloy electrodes

Fig. 4 shows the electrochemical discharge capacities at 293 K for electrodes made from $Ti_{33}V_{20}Cr_{47}$ alloy and $Ti_{33}V_{20}Cr_{47} + 4\%$Pd at discharge current of 60 mA g$^{-1}$. The better characteristic of potential plateau demonstrated a great improvement on discharge performance when adding Pd particles to $Ti_{33}V_{20}Cr_{47}$ alloy. The discharge capacity for $Ti_{33}V_{20}Cr_{47}$ alloy electrode was only 12 mAh g$^{-1}$, while the $Ti_{33}V_{20}Cr_{47} + 4\%$Pd alloy showed a much higher discharge capacity up to 225 mAh g$^{-1}$, and 90% of total discharge capacity could be obtained below −1 V. The intrinsic discharge capacity of the $Ti_{33}V_{20}Cr_{47}$ alloy was impulsed