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TiO_2 Fabricated from Vietnamese Ilmenit Applying for Battery Anode

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Abstract: In this study, TiO_2 was fabricated from Vietnamese ilmenite using plasma treatment. It was used as the active material in the metal-air battery to find the better anode material for metal-air battery. The physical and electrochemical properties of TiO_2 samples were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) and cyclic voltammetry (CV). The obtained results showed that pure TiO_2 fine powder was successfully fabricated by plasma treatment and it can be used as the anode material in metal-air batteries. The influence of Acetylene Black (AB) additive on the electrochemical behaviors of TiO_2/AB and TiO_2/Fe_2O_3/AB electrodes were investigated. The prepared TiO_2 could be a promising candidate for a metal/air battery anode.

Keywords: TiO_2 particles, plasma, carbon additive, TiO_2-Fe_2O_3/AB composite electrode, Fe/air battery anode.

1. Introduction

As a versatile functional material, titanium dioxide (TiO_2) has a wide range of applications, such as solar cells, photocatalytic water splitting, gas sensing, and so on [1-3]. Besides that, TiO_2-based materials are of great interest for energy storage and conversion devices, in particular rechargeable lithium ion batteries (LIBs). Due to its excellent advantages of low cost, nontoxicity, environmentally benign, thermally and chemically stability, TiO_2 has been developed to be a promising anode material for LIBs [4]. Lithium-ion batteries are some of the most promising batteries because of their high energy density, low maintenance and relatively low self-discharge [5-7].

However, during searching for energy storage systems with higher energy density, metal/air batteries have received great interest. Several metal/ air batteries have been studied, such as lithiume air, sodiume air, zince air, magnesiume air, aluminume air, iron air and potassiume air. All the above

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batteries have very high theoretical energy density about 2- 10 folds higher than that of lithium-ion batteries [8-9].

Therefore, in the present study, TiO_2 obtained from Vietnamese ilmenite using plasma treatment was used as the active material of negative electrodes for Fe-air batteries. Nanocarbon was used as an additive material for improving the electrical conductivity and the cycleability of TiO_2 electrode. The electrochemical properties of the prepared TiO_2 and the effect of carbon on the electrochemical properties of TiO_2 electrode were investigated to find the best suitable material for Fe-air battery anode.

2. Experimental

Refined ilmenite (Ninh Thuan - Vietnam) was treated by plasma to obtain the relative pure TiO_2. It was used as the active material for preparing negative electrodes in Fe-air battery.

Acetylene black (AB, Denki Kagaku Co. Ltd.) was used as the carbon additive to enhance the conductivity of TiO_2/C electrodes. All chemicals purchased from commercial sources were analytical grade and were used as received without additional reprocessing.

The titanium compound obtained was identified to be TiO_2 by X-ray diffraction (XRD). The morphology of the as-prepared TiO_2 powder was observed scanning electron microscopy (SEM).

To determine the electrochemical behavior of as-fabricated TiO_2, we prepared two electrode sheets, containing and free TiO_2. The electrode sheeting free TiO_2 was prepared by mixing 45 wt.% TiO_2 and 10 wt.% polytetrafluoroethylene (PTFE; Daikin Co.), followed by rolling. The electrode sheeting containing Fe_2O_3 was fabricated at a ratio of TiO_2:Fe_2O_3: PTFE = 45:45:10 wt. %. Each electrode was formed into a 1 cm-diameter pellet.

To obtain the effect of carbon additive, the TiO_2/AB and TiO_2/Fe_2O_3/AB electrode sheets were prepared by the same procedure with the mixing ratio of TiO_2:AB: PTFE = 45:45:10 wt. % and TiO_2:Fe_2O_3:AB:PTFE = 40:40:10:10 wt. %. Bothe TiO_2/AB and TiO_2/Fe_2O_3/AB electrodes were made into a pellet of 1 cm diameter.

To investigate the electrochemical properties of prepared TiO_2 and effect of AB additive on the electrochemical properties of the TiO_2/AB and TiO_2/Fe_2O_3/AB electrodes, cyclic voltammetry (CV) were carried out in three-electrode glass cells with TiO_2 or TiO_2/Fe_2O_3 or TiO_2/AB or TiO_2/Fe_2O_3/AB electrode as the working electrode, Pt mesh as the counter electrode, and Hg/HgO as the reference electrode. The electrolyte was 8 mol dm^{-3} KOH aqueous solution. CV measurements were taken at a scan rate of 5 mV s^{-1} and within a range of −1.3 V to −0.1 V. In all electrochemical measurements, we used fresh electrodes without pre-cycling.

3. Results and discussion

Figure 1 shows the XRD pattern of the TiO_2 fabricated from Vietnamese ilmenite using plasma treatment. It can be seen that the characteristic peaks for TiO_2 are consistent with the database in CSD file (ICSD No.24276) and it revealed that the resultant particles were pure TiO_2.

To obtain the morphology and particles size of TiO_2 fabricated from Vietnamese ilmenite using plasma treatment, SEM measurement was carried out and the result is showed in Figure 2. It is clear that the TiO_2 particles have similar morphology and shape and they look like the balls. Their particle size is relative uniform and less than 500 nm.

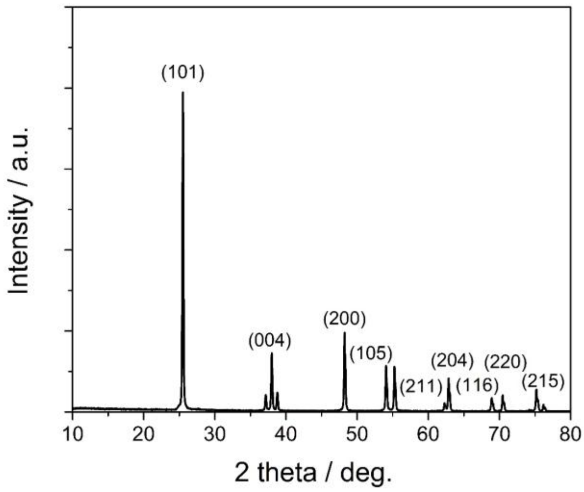

Figure 1. XRD pattern of the TiO_2

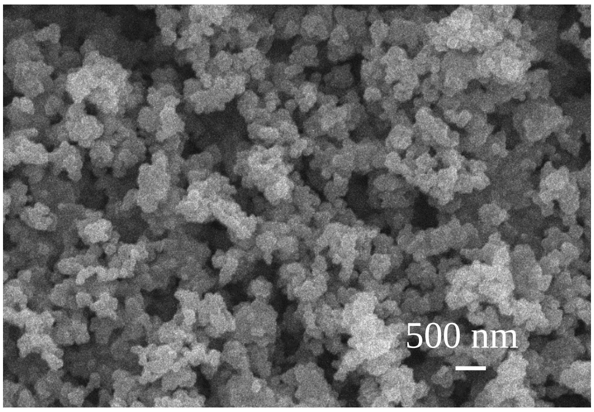

Figure 2. SEM image of TiO_2

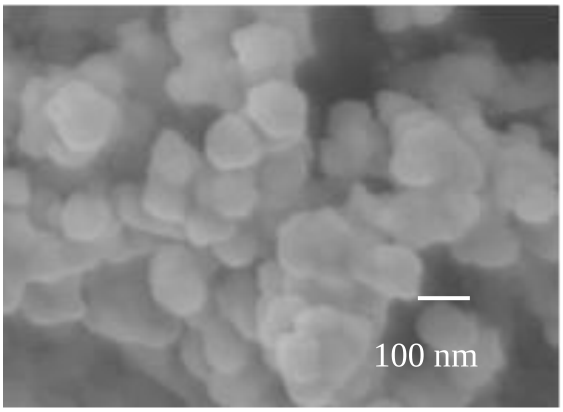

Figure 3. SEM image of Acetylene black (AB)

Figure 3 depicts the SEM image of Acetylene black (AB). The average diameter of AB is about 100 nm. The shape of AB is relative uniform and particles also look like the balls. It is used as an additive to electrode to enhance the conductivity of TiO_2 and TiO_2-Fe_2O_3 electrodes. When TiO_2 is used as electrode active material, in the present of AB additive, TiO_2/AB and TiO_2-Fe_2O_3/AB electrodes are expected to provide the better cycleability and the higher capacity than TiO_2 electrode.

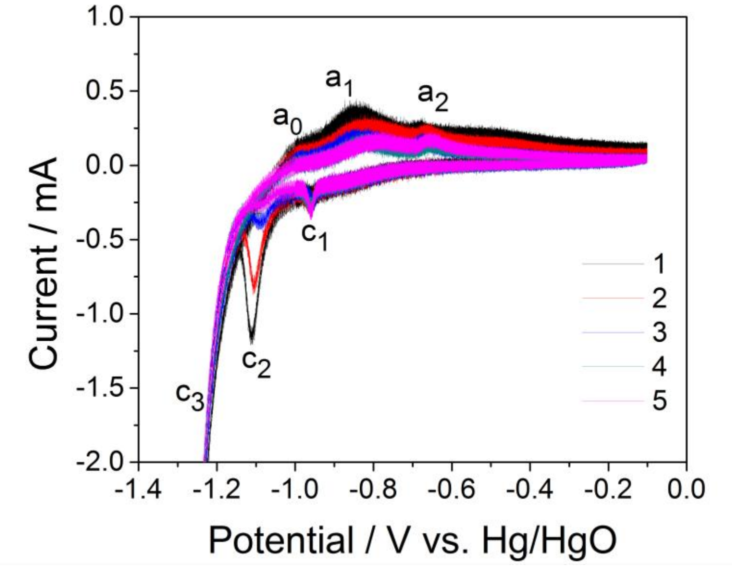

Figure 4. Cyclic voltammogams of a TiO_2 composite electrode with TiO_2:PTFE = 90:10 wt.% in KOH aqueous solution.

The cyclic voltammograms of the TiO_2 electrode are shown in Figure 4. Several peaks were observed, including the oxidation peaks at around –0.95V (a_0), –0.8V (a_1) and –0.65V (a_2) on the forward scan and the corresponding reduction peaks at around –0.95V (c_1) and –1.1 V (c_2) on the backward scan. The a_0 peak was attributed to oxidation of Ti to Ti(I) and c_3 peak was hydrogen evolution. The reduction peak c_2 was separated from hydrogen evolution (c_3). The first and second anodic peaks (a_1 and a_2) can be attributed to oxidation of Ti to Ti (II) (a_1) and Ti (II)/Ti (III) and Ti (III)/Ti (IV) (a_2) while cathodic peaks (c_1 and c_2) correspond to the reduction of Ti (IV)/Ti (III) and Ti (III)/Ti (II) (c_1) and Ti (II)/Ti (c_2), respectively. Thus, a_1 and c_2 correspond Ti/Ti(II) redox couple while a_2 and c_1 correspond Ti (II)/Ti (III) and Ti (III)/Ti (IV) redox couple. With further cycling, the redox current under these peaks was decreased. This could be ascribed to the passive film nature of the Ti^{4+} active material forming during cycling.

To make clear the effect of the cacbon additive on the electrochemical behavior of the TiO_2 electrode, CV measurement was carried out for the TiO_2/AB electrode, and the result is presented in Figure 5. The redox couples of Ti/Ti (II) and Ti (II)/Ti (III) occurred at around −0.85 V (a_1) on the oxidation and −0.9 V (c_1) on the reduction process. The anodic peak a_0 was observed at around -0.95V and the cathodic peak c_2 was unobservable. Comparison with CV profiles of the TiO_2 composite electrode free AB additive (Fig. 4), it can be seen that in the case of TiO_2/AB electrode (Fig. 5) only one couple peak of Ti /Ti (II) and Ti (II)/Ti (III) (a_1/c_1) occurred but the current under these peaks was larger than that of the TiO_2 electrode. However, the anodic peak a_1 occurred at more negative potential than that at TiO_2 electrode. This could be ascribed to the passive film nature of the Ti^{4+} active material formed during discharge process, which would inhibit the Ti/Ti(II), and Ti (II)/Ti (III) redox couples, and resulting in an increased overpotential. Thus, the present of AB in TiO_2 electrode might cause the shift of redox peaks toward to more negative potentials and lead to the overlap of hydrogen evolution c_3 on the reduction peak c_2. With further cycling, the current under these peaks gradually decreased but the decreasing rate at TiO_2/AB electrode was smaller than that at TiO_2 electrode. The difference in the CV profiles of TiO_2 and TiO_2/AB composite electrodes revealed the influence of the AB additive on the electrochemical properties of TiO_2 electrode.

These results suggest that the cycleability of TiO_2/AB composite electrode was improved significantly by AB additive.

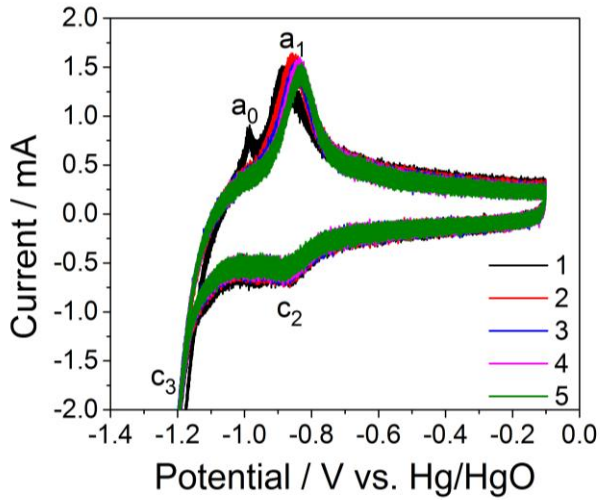

Figure 5. Cyclic voltammogams of a TiO_2/AB composite electrode with TiO_2:AB:PTFE = 45:45:10 wt.% in KOH aqueous solution.

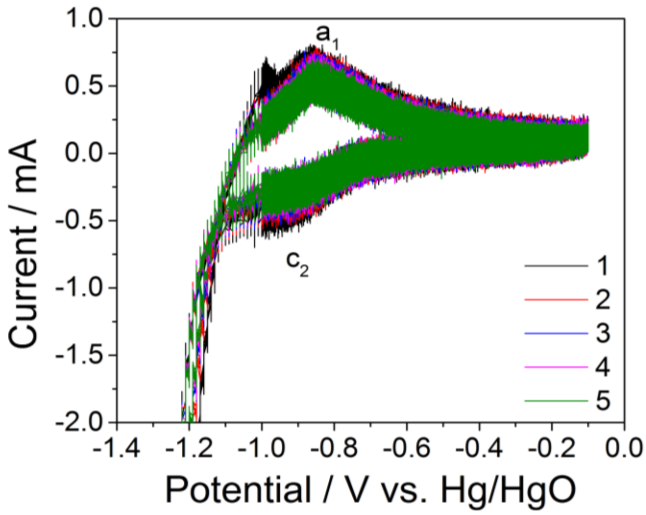

Figure 6. Cyclic voltammogams of a Fe_2O_3-TiO_2 composite electrode with Fe_2O_3:TiO_2:PTFE = 45:45:10 wt.% in KOH aqueous solution.

To find the better electrode material for Fe-air battery anode, the mixture of Fe_2O_3 (Walko, nanoparticles) and TiO_2 were used as the active material and, their CV result is presented in Fig. 6. Only a small redox couple peak a_1, c_2 was observed at around −0.80 V (a_1) and −0.9 V (c_2) together with hydrogen evolution peak c_3 on TiO_2-Fe_2O_3 electrode and the current under these peaks is rather small. Comparison with CV result of TiO_2 electrode (Fig. 4), it is clear that the electrode using prepared TiO_2 showed the better redox reaction than TiO_2-Fe_2O_3 (Fig. 6). It may be due to the commercial Fe_2O_3 have smaller particle size than TiO_2, consequently with the same wt.% of binder, the contact between the particles in TiO_2-Fe_2O_3 electrode was loosen and thus it gave larger internal resistance than TiO_2 electrode.

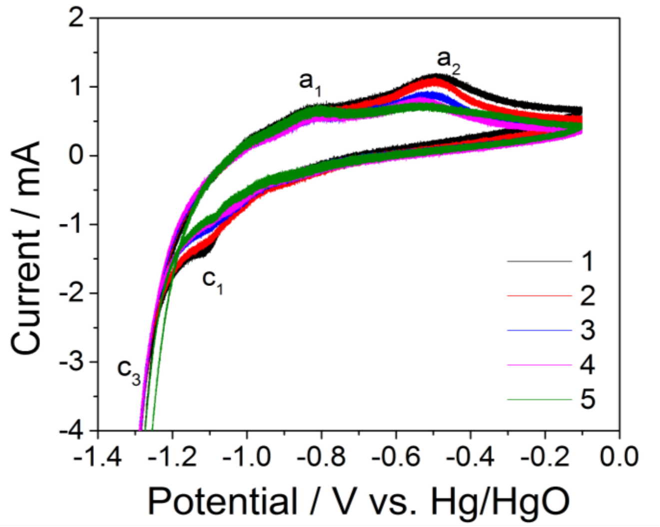

Figure 7. Cyclic voltammogams of a Fe_2O_3-TiO_2/AB composite electrode with Fe_2O_3:TiO_2:AB:PTFE=40:40:10:10 wt.%

Figure 7 show in the cyclic voltammograms of the TiO_2-Fe_2O_3/AB composite electrode. Two oxidation peaks were observed at around −0.8V (a_1) and −0.5 V (a_2) while only one reduction peak occurred around −1.1V (c_1), respectively. The reduction peak c_2 was unobservable due to the superimposed in hydrogen evolution (c_3).

Comparison CV results of TiO_2-Fe_2O_3/AB (Fig. 7) and TiO_2-Fe_2O_3 (Fig. 6) electrodes we can see clearly the positive effect of AB on the cycleability and cycle performance of TiO_2-Fe_2O_3 electrode.

In the case of TiO_2/AB electrode (Fig. 5), although AB additive improved its cycleability but TiO_2-Fe_2O_3/AB showed better cycleability and higher capacity as evidenced by the occurring of two oxidation peaks a_1, a_2 instead of only oxidation peak a_1 in TiO_2/AB electrode and provided larger redox current than TiO_2/AB electrode.

4. Conclusion

TiO_2 fine powder was successfully fabricated from Vietnamese ilmenite using plasma treatment. The SEM results showed that small TiO_2 particles aggregated to form large particles in micrometer scale. The electrochemical properties of prepared TiO_2 in alkaline solution were investigated. The obtained results revealed that these TiO_2 materials can be used for the anode in metal-air batteries. AB additive showed the significantly effects on the electrochemical properties of both the TiO_2/AB and the TiO_2-Fe_2O_3/AB electrodes improving the cycleability and reaction rate of TiO_2. With further investigation to find the optimal preparation condition, the TiO_2 fine powder with uniform particles is expected to be a potential candidate for use in metal/air battery anode.

Acknowledgments

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References

[1] B. O'Regan, M. Gratzel, A Low-Cost, High-Efficiency Solar Cell Based on Dye-sensitized Colloidal TiO_2 Films. Nature *353* (1991**)** 737.

[2] S. U. M. Khan, M. Al-Shahry, W. B. Ingler, Efficient Photochemical Water Splitting by a Chemically Modified n-TiO_2, Science 297 (2002**)** 2243.

[3] X. Chen, S. S. Mao, Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications, Chem. Rev. 107 **(**2007**)** 2891.

[4] D. Deng, M. G. Kim, J. Y. Lee, J. Cho, Green Energy Storage Materials: Nanostructured TiO_2 and Sn-Based Anodes for Lithium-Ion Batteries, Energ. Environ. Sci. 2 (2009**)** 818.

[5] B. Luo, S. Liu, L. Zhi, Chemical approaches toward graphene-based nanomaterials and their applications in energy-related areas, Small 8 (2012) 630.

[6] D. Liu, G. Cao, Engineering nanostructured electrodes and fabrication of film electrodes for efficient lithium ion intercalation, Energy Environ. Sci. 3 (2010) 1218.

[7] P. G. Bruce, B. Scrosati, J. M. Tarascon, Nanomaterials for rechargeable lithium batteries, Angewandte Chemie Int. Ed. 47 (2008) 2930.

[8] D. Linden, T.B. Reddy, Handbook of Batteries, McGraw-Hill Professional, 2001.

[9] Z. Xin, W.Xin-Gai, X. Zhaojun, Z. Zhen, Recent progress in rechargeable alkali metal–air batteries, Green Energy & Environment 1 (2016) 4.