Carbon Nanofibers Prepared with Ni-MgO Catalyst Treated by Mechanochemical Process and Their Application as Catalyst Support Material for PEMFC

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Abstract

Mixture of $Ni(OH)_2$-$Mg(OH)_2$ used as the precursor of catalyst was treated by mechnochemical(MC) and hand grinding process. Carbon nanofibers(CNF) were prepared using CVD process with the above prepared catalyst. CNFs with a uniform diameter were obtained with MC process treated catalyst, and the diameter could be controlled by tuning the grinding time. CNF bundles with close coalescence were produced with MC treated catalyst. After purification of CNFs and loading with Pt, they were used in fuel cell as the cathode catalyst support. The performance with carbon nanofibers prepared using ground mixture was found to be better than that prepared using unground mixture, which is attributed to the homogeneous CNFs with small diameter and specific interaction between Pt and CNFs.

Introduction

Carbon nanofibers(CNF) have excellent electric conductivity, absorbability and mechanochemical property applicable to polymer reinforcement [1], electrode materials[2], catalyst support materials [3-5], and energy storage[6-8]. CNFs can present large number of edges, which are active sites for chemical or physical interaction, particularly adsorption. CNFs supporting Pt metal clusters with high and uniform dispersion will find the most suitable application as the catalyst support materials in fuel cell systems.

The growth of CNFs by a catalytic pyrolysis of hydrocarbon gases requires the transition metal catalyst such as Ni, Co, Fe, etc. It is possible to tailor the growth of CNFs to generate structure of a desired conformation by choosing the catalyst and controlling the reaction conditions carefully. In this study, mechnochemical process was used to treat the precursor of catalyst, which was speculated to govern the structure of as-grown CNFs. And the as-prepared CNFs were applied in the fuel cell as the catalyst support materials in cathodes.

Experimental

$Ni(OH)_2$ and $Mg(OH)_2$ were used as the staring materials to prepare catalyst, and the mol ratio of Ni and Mg was 1:1. They were well mixed by grinding under dry condition using a mixer mill(MM200,Retsch). The grinding was done at approximately 1800rpm, and the duration of grinding was 120-360 min. In order to compare, $Ni(OH)_2$ and $Mg(OH)_2$ mixtures were also ground in ethanol with an agate mortar and pestle. The catalysts were labeled as MC and MP, respectively.

Carbon nanofibers were grown by thermal CVD in quartz-tube electric furnace with C_2H_2 as a carbon source. An argon stream was first introduced into when heating from room temperature to 500℃. Then H_2 of 100 sccm flowed to reduce the surface of mixture to obtain Ni particle used as a catalytic active site for 30min. Next, C_2H_2 gas at 10 sccm and H_2 gas at 100 sccm were simultaneously flowed for 30 min to prepare CNFs. Finally, the sample was cooled down to room temperature under an argon stream.

The as-grown CNFs were purified with HNO_3 and HCl to remove Ni and MgO. The nanofibers were stirred in 3M HNO_3 solution and refluxed for 24h at 60℃, then they were stirred in 5M HCl and refluxed for 6h at 120℃. Finally the purified nanofibers were washed using distilled water and isopropyl alcohol.

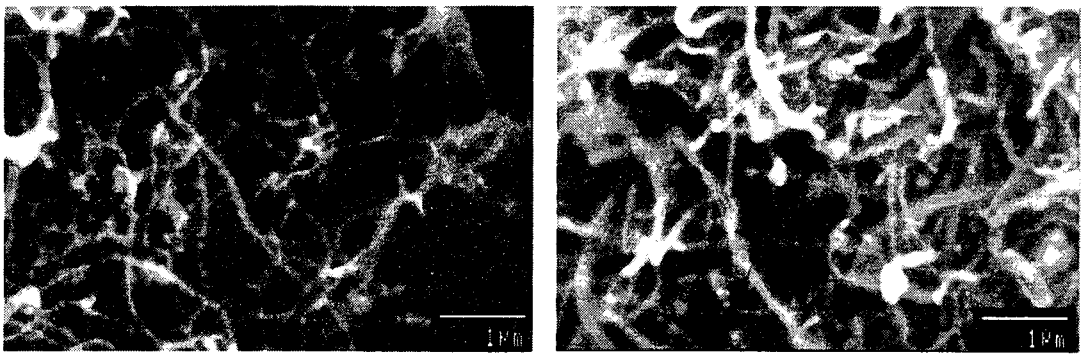
Morphology of as-grown carbon nanofibres and Pt loaded carbon nanofibers was observed by the scanning electron microscope (SEM, JSM-840A and Phillips XL 30S FEG).

Purified carbon nanofibers were impregnated with 1% H_2PtCl_6 in distilled water. A solution of 1% $NaBH_4$ reducing agent was added with stirring. Then the mixture was dried, cooled and washed repeatedly with distilled water. Finally the Pt catalyst powder was heated overnight at 80℃ in an air-oven.

Catalyst ink was prepared by mixing Nafion(5wt.%) solution with 20% Pt/carbon nanofibers and isopropyl alcohol. The ink was applied on carbon paper based gas diffusion layer(GDL 10-H, SGL Carbon Group Technologies Sigracet) by brush method. It was dried at 80℃ for 30 minutes. Platinum loading was maintained at 0.5mg/cm^2 on both the anode and the cathode. The electrodes with 5 cm^2 area were hot bonded on Nafion 1035 at 130℃ at a pressure of 2000 psig for 1 minute. Fuel cell was assembled using the membrane electrode assembly(MEA) and was tested at 80℃ using H_2 and O_2 reactants at a pressure of 1 atm. The humidification temperatures of hydrogen and oxygen were maintained at 90℃ and 85℃, respectively. The current-voltage(I-V) characteristics were evaluated using WonATech battery cycler.

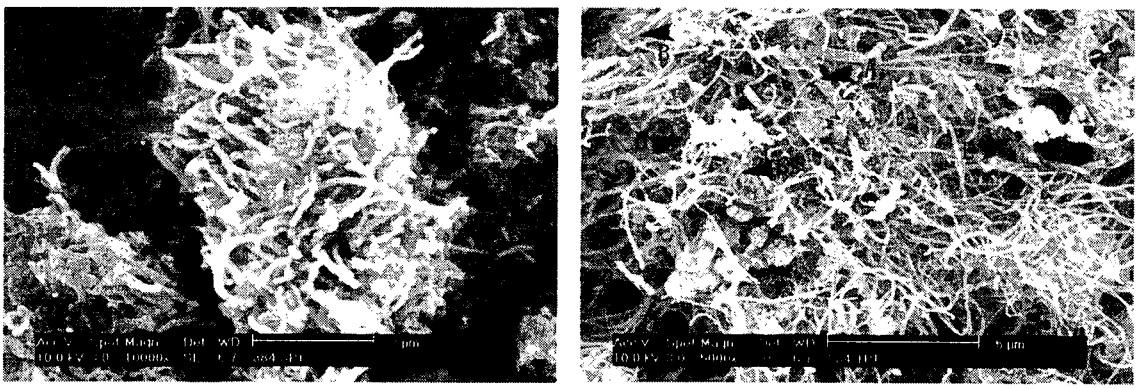
Results and Discussion

Fig.1 shows the SEM images of as-grown nanofibers. It was shown that homogeneous CNFs with diameter 50-80nm were produced with the MC catalyst. However, CNFs prepared with MP catalyst were nonhomogeneous and had a bigger diameter. Mechnochemical process using a high-energy ball-mill has been widely used for preparing nonequilibrium materials like nanocrystalline and amorphous materials. It is an effective way to rapidly refine the particle microstructure, i.e., grain size or crystallite size, during milling [9-10]. It is believed that the homogeneous distribution of CNFs is due to the homogeneous distribution of Ni particles with the mechanochemical process, and finer CNFs are attributed to refine by grinding. Therefore homogeneous diameter and controlled size CNFs can be obtained with catalyst prepared by mechnochemcal process.



(a) MC catalyst (b) MP catalyst

Fig.1 SEM image of as-grown CNFs



(a) MC catalyst (b) MP catalyst

Fig.2 SEM images of the CNFs loaded Pt

Fig.2 shows the SEM images of the CNFs loaded Pt. It was shown that CNFs are homogeneous and the diameter is about 75nm, and there is no Pt agglomeration found for MC catalyst. However, there are three different diameter CNFs for MP catalyst. It is about 400nm, 150nm and 75nm for the CNFs in site A, B and C. Pt is not distributed uniformly on the CNFs, instead agglomerated (site D and E). Fig.3 is the magnified photo of Fig.2(a). It can be seen that CNFs are homogeneous bundles. It would be the defects or disorder in the boundaries of CNF bundles that help interaction of Pt with CNFs.

Fig.4 shows the I-V characteristics of PEMFC electrodes using carbon nanofibers prepared by two different samples as described earlier, used as cathode catalyst support. It is clearly seen that the performance of electrode prepared using carbon nanofibers with MC catalyst is better than that prepared using MP catalyst. At a current density of 0.5A/cm^2, the fuel cell voltage using CNFs prepared with MC catalyst was 0.55V, while that using CNFs prepared with MP catalyst was 0.44V. The better performance could be attributed to the homogeneous CNF with small diameter prepared using ground mixture, as well as to the specific interaction between Pt and CNFs.

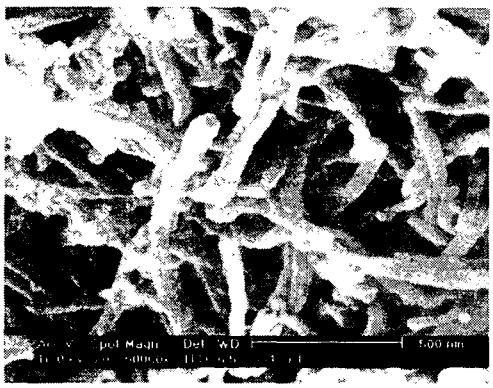


Fig.3 Magnified SEM image of the loading Pt CNFs prepared with MC catalyst

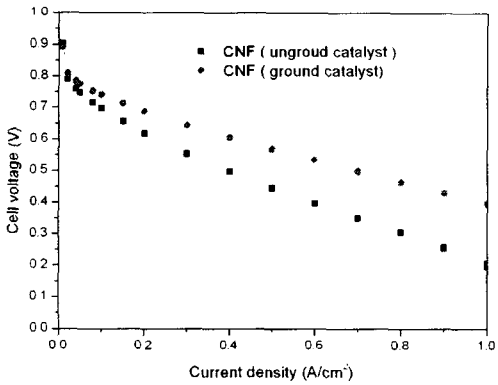


Fig.4 Comparative performance of catalyst on different CNF supports using Nafion 1035

Conclusions

Homogeneous CNFs with diameter 50-80nm were obtained using catalyst prepared by MC process. MC catalyst can produce homogeneous CNF bundles. Pt was loaded homogeneously on the CNFs prepared with MC catalyst.

CNFs prepared by MC catalyst used as cathode catalyst support gave better fuel cell performance compared to that prepared with MP catalyst. The superior performance could be attributed to the uniform CNFs with small diameter, as well as the specific interaction between Pt and CNFs.

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References

1. Wang,X.; Wang,S.; Chung, D.D.L. J.Mater.Sci. 1999,34,2703
2. Endo,E., Kim Y.A., Hayashi T., Nishimura K, Matusita T., Miyashiya K, Dresselhaus M.S. Carbon 2001,39,1287
3. Rodriguez,N.M.; Kim,M.S.;Baker,R.T.K. J.Phys.Chem. 1994,98,13108
4. Park,C.; Baker,R.T.K. J.Phys.Chem.B 1998,102,5168
5. Baker,R.T.K.; Laubernds,K.; Wootsch,A.; Paal,Z. J.Catal. 2000,193,165
6. Park,C.; Anderson,P.E.; Chambers,A.; Tan,C.D,; Hidalgo,R.; Rodriguez,N.M. J.Phys.Chem.B 1999,103,10572
7. Fan,Y.Y.; Liao,B.; Liu,M.; Wei,Y.L.; Lu,M.Q.; Cheng,H.M. Crabon 1999,37,1649
8. Gupta,B.K.;Srivastava,O.N. Int.J.Hydrogen Energy 2000,25,825
9. C.Surayanarayana, Prog Materi Sci 46(2001) 1
10. C.C.Koch, Nanostructureed Mater. 9 (1997) 13