SUPERCRITICAL CO_2 DRYING FOR PREPARING NOVEL METAL-DOPED MELAMINE AEROGELS

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ABSTRACT
Supercritical CO_2 drying was used for preparing novel metal-doped melamine aerogels. 2,6-dihydroxy-4-methylbenzoic acid, melamine and formaldehyde were used for making aerogels by sol-gel polymerization. The materials were doped with cobalt by using the ion-exchange method.

INTRODUCTION
The right drying method is necessary for aerogel preparation. Supercritical CO_2 drying is described as the best method for preparing these materials, with the least shrinkage occurring during drying and thus keeping the porous structure of the gel intact. This method enables to prepare aerogels with fully interconnected mesopores.
N-doped carbon materials have been reported as good catalysts for oxygen reduction reaction [1]. Melamine has a high nitrogen content and has been used before for making N-doped carbon aerogels [2]. The incorporation of cobalt into the catalyst would further increase the catalytic activity [3].
We hereby propose a new method for preparing cobalt and nitrogen containing carbon aerogels by using the ion-exchange method for doping with cobalt [4].

MATERIALS AND METHODS
Aerogels were prepared by sol-gel polymerization, using melamine and 2,6-dihydroxy-4-methylbenzoic acid with formaldehyde as precusors. After that the cobalt ions were introduced into the gels through the ion-exchange method. The resulting Co-doped melamine gels were dried by using supercritical CO_2 drying and also freeze-drying for comparison. Carbonization was done in N_2 atmosphere at temperature 700-900 °C.
The resulting supercritically dried materials were analysed with atom absorption spectroscopy, N_2-adsorption analysis and scanning electron microscopy (SEM).

RESULTS
The supercritical drying method used in this study for a typical cobalt doped melamine gel resulted in 17% shrinkage in the diameter of the monolithic sample and the density was 0,33 g/cm^3. In comparison freeze-drying lead to much more shrinkage (43%).
The prepared carbon aerogels were mostly mesoporous and contained up to 5 wt% of cobalt and 23 wt% of nitrogen. The elemental composition of the materials can be changed by varying the composition of the gel.
Scanning electron microscopy pictures of carbon aerogel pyrolysed at 800 °C is shown in figure 1.

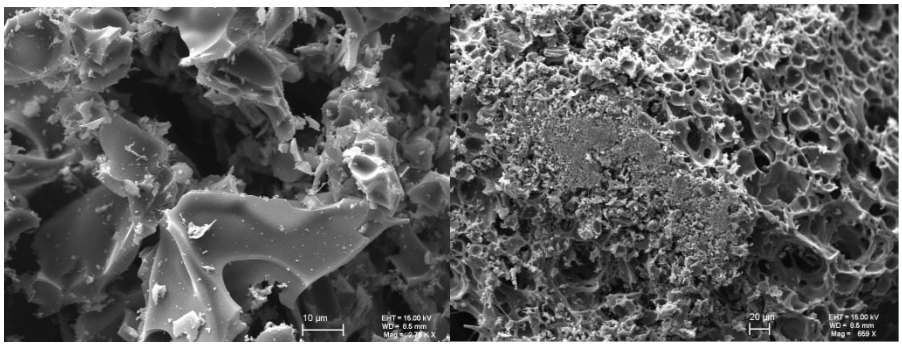

Figure 1. SEM pictures of carbon aerogels

CONCLUSION

In this study the preparation method for cobalt-doped melamine aerogel is developed and the material is characterized. The cobalt and nitrogen containing carbon aerogel is a promising material as an electrochemical catalyst in oxygen reduction reaction.

REFERENCES

[1] Wang, H., Maiyalagan, T., Wang, X. ACS Catalysis,Vol. 2, 2012, p. 781-794.
[2] Wei, Y., Shengzhou, C., Weiming, L. Int. J. Of Power Energy, Vol. 37, 2012, p. 942-945.
[3] Bezerra, C., Zhang, L., Lee, K., Liu, H., Marques, A., Marque, E., et al. Electrochim Acta, Vol. 53, 2008, p. 4937-4951.
[4] Baumann, T., Fox, G.A., Satcher, J.H., Yoshizawa, N., Fu, R., Dresselhaus, M.S. Langmuir, Vol. 18, 2002, p. 7073-7076.