Pt NANOCLUSTERS ON CARBON NANOMATERIALS FOR HYDROGEN FUEL CELLS

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Introduction

Pt superfine clusters on conductive supports are effective catalysts of redox reactions proceeding in fuel cells. High specific surface, support conductivity, high dispersity (nanosizes of clusters Pt) and their strong fixation on a surface are necessary criterion of preparation of the effective catalyst. From these points of view carbon nanomaterials (CNM) for example single- (SWNT) and multiwall (MWNT) nanotubes, nanofibers (CNF) and x-ray amorphous carbon (AC) can be a successful supports of Pt clusters.

Results and discussion

Crude CNM: SWNT (Ni-Y catalyst) [1], MWNT [2] and AC [3] obtained by arc method and CNF prepared by C_2H_4 - H_2 mixture pyrolysis over $LaNi_5$ at 700 ºC [4] inclusive carbon fragments without function groups are hydrophobic and as graphite does not form a compounds with Pt ions. The specific surface (BET, N_2) is 380 $m^2 \cdot g^{-1}$ for SWNT and 287 $m^2 \cdot g^{-1}$ for AC. The carbon atoms in these fragments are bound with each other by different types of bonds. In particular, in pattern of SWNT, MWNT and CNF there are in the main graphene fragments with aromatic bonds. In AC single and non-conjugated double bonds are alternated. These discrepancies in CNM pattern are shown on reactivity in air thermogravimetry (fig. 1).

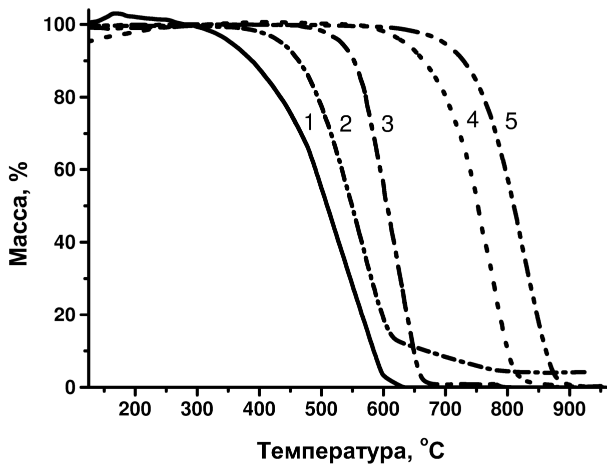

Fig.1. TG curve for carbon nanomaterials: 1 – AC, 2 – SWNT, 3 – CNF, 4 – MWNT, 5 – graphite.

For strong Pt fixation on CNM surface it is necessary to introduce function groups, preferable from ones are -COOH, -OH and quinoid. The diversity of carbon allotropic forms and types of bonds between carbon atoms causes the different approaches to inculcation of a function groups on CNM surface.

In particular, into SWNT and MWNT, which ones represent the convolute graphene planars, function groups, as well as in case of graphite, are possible to introduce by treatment by strong oxidants such as HNO_3 - H_2SO_4. CNF are more reactive, though at their pattern also are presented by graphene planar stacks. One oxygen atom per 22 carbon atoms can be introduced into CNF by mixture HNO_3 - H_2SO_4 oxidation, in comparison with SWNT - 1 O atom per 37 C atoms and with MWNT - 1 O atom per 97 C atoms.

More wide opportunities for Pt fixation are available in the case of AC. The H_2PtCl_6 treatment of AC enables Pt addition to double bond without pretreatment. Bromination [3] and the alcaline hydrolysis allows to enter one such group per 7-8 C atoms.

The introducing of function groups into SWNT, MWNT and CNF destroys their aromatic bonds and decreases their conductivity therefore MWNT, wherein conductivity is ensured interior not affected by treatment layers, is suitable support. Really, at total concentration one O atom pre 97 C atoms, on a surface is present more than 1 O atom per 25 C atoms.

After function groups introduction on a CNM surface the platinum can be applied from $PtCl_4^{2-}$ or $PtCl_6^{2-}$ ions solutions. Pt $(NO_2)_4^{2-}$, $Pt(OH)_6^{2-}$ ions and oter Pt compounds formed with these groups tenuous bridging -O-O- and only donor-acceptor bonds for this purpose are unsuitable. At interaction $PtCl_4^{2-}$ or $PtCl_6^{2-}$ with -OH or -COOH groups HCl is yielded, therefore introducing in a reaction mixture of base, which is not generates $Pt(OH)_6^{2-}$, is necessary. In it difference of our approach against papers devoted to this [5, 6].

CNM with supported Pt (II, IV) for transformation into the active form the reductions up to Pt (0) require. For this purpose not all reducing agents are applicable. In particular, as a result of reduction Pt (IV) supported on SWNT, MWNT or CNF by $HCOO^-$ ion at Pt content

12 % mass. we obtain Pt (0) clusters dimensioned 10-20 nm (fig. 2-4). It is necessary to mark, that the sizes of Pt clusters of traditional catalysts 10 % Pt/C are more (100-200 nm).

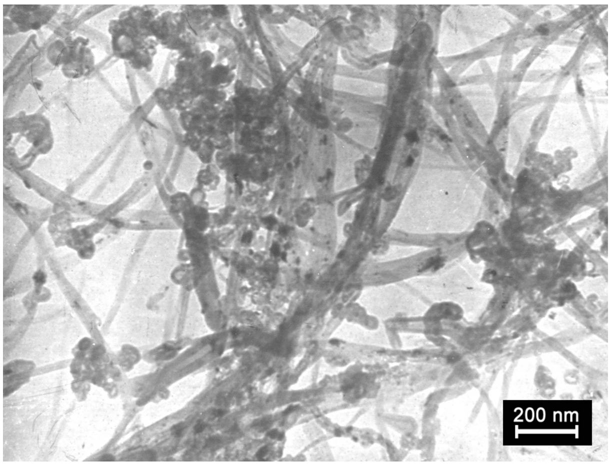

Fig. 2. TEM image of 12 % Pt/SWNT.

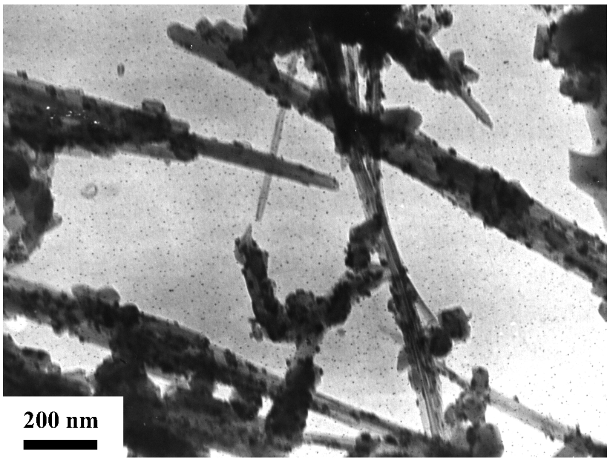

Fig. 3. TEM image of 12 %Pt/MNT.

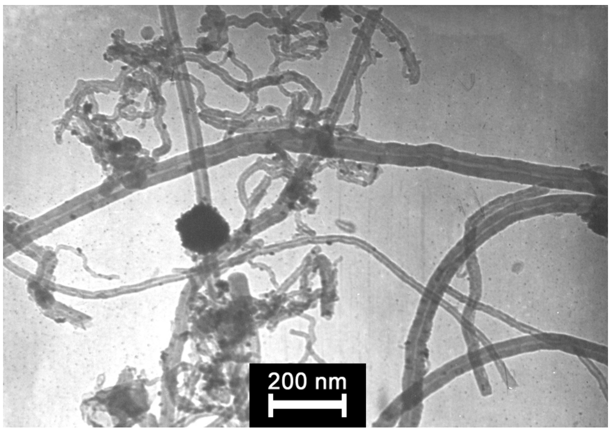

Fig. 4. TEM image of 12 %Pt/CNF.

Hydrogen reduction of Pt (II, IV)/CNM yields a pyrophoric forms which are unsuitable for use in fuel cells. The reduction by BH_4^-, $N_2H_6^{2+}$, NH_2OH or its salts generate boride or nitride forms required hydrogen activations and, as stated above, are unsuitable for use in fuel cells.

Summary

The hydroxyl and carboxyl groups introdused into CNM are suitable for platinum applying from $PtCl_6^{2-}$ ion on CNM. The applying is necessary realized in presence of base which is not converting $PtCl_6^{2-}$ ion to $Pt(OH)_6^{2-}$ one.

The samples obtained by reduction of Pt (II, IV)/CNM by organic reducers, in particular, formiate - ion can be used as the catalysts in fuel cells.

The detailed study of CNM constitution with allowance for of reduction conversions Pt (II, IV) allows to realize directional looking up of methods of preparation of platinum catalysts for redox reactions in hydrogen fuel cells.

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