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The Modification of Surface Characteristics Of the Carbon Electrode Binder

by

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DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lift by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

The Modification of Surface Characteristics Of the Carbon Electrode Binder

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SUMMARY

Hard pitch is extensively used as binder, in the production of carbon electrode for electrochemical technology because it is rather cheap and easily obtainable. However the surface area of the carbon produced from this material is considerably high which affect the performance and the consumption of the electrode directly.

The following article is about to find out whether it would be possible to use polybvinylchloride and polyfurfurylalcohol as binder modifiers to reduce the surface area of the hard pitch carbon, It was found that 15 % of polyfurfurylalcohol reduces the surface area from 89.5 $m^2.g^{-1}$ in hard pitch-petroleum coke carbon, down to 13.3 $m^2.g^{-1}$ in the carbon obrtained from the triple mixture of hard pitch, petroleum coke and polyfurfurylalcohol. A homogeneous pore structure was developed under the working condition by addition of polyfurfurylalcohol, was also found.

Introduction

The microporosity of the carbon electrodes used in the electrochemical and electrometallurgical industries has a great influence on the

consumption of electrode. Conventionally, petroleum coke is used as filler and high temperature coal coking tar distillation residue hard pitch is used as binder in the production of the carbon electrode[1]. After being plasticised by heat, hard pitch is mixed with suitable amount of pertroleum coke which is followed by molding and baking. In some cases by subjecting to high temperature heat treatment molded and baked carbon electrodes are graphitised.

Not only the binder but also the filling material influence the production and the performance of the carbon electrodes. Since petroleum considerably cheaper than coal coke, it is preferred in the production of carbon electrodes. By definition, petroleum coke is a petroleum refining residue containing sulphur, ash and volatiles in low proportions.[2] The performance of the electrode depends closely on the chemical composition, specific surface area, adsorption capacity and chemical reactivity of the petroleum coke used in production.

In order to improve electrode performance and to reduce the consumption of the electrode it is necessary to alter the surface characteristics of the binder carbon by using a modifier. For this purpose it is thought that it may be possible to use synthetic polymers. The synthetic polymer that is intended to be used as binder modifier, has to be carbonising type in the first place instead of being disintegrated to its monomer by heat treatment. In addition to this it has to be plasticised hence the available micropores can be blocked.

The binder and the modifier must be fluid at lowest temperature possible. On the other hand, during the preparation of binder filler paste the viscosity has to stay high enough at the highest paste preparation temperature. To prevent binder filler segregation, binder ought to penetrate through the filler particles and must have enough wettability.

During the carbonisation, since the excess gas evolution alters surface structure significantly the gas production must be kept at its lowest level possible.[3]

Thus the binder or the modifier used in the production of the carbon electrode must have many requirements which are effective directly or indirectly on the performance of the electrode. To reduce the influence of the above discussed factors to a minimal level, the use some synthetic polymers was considered. Thus, this article is concerned to find out whether polyvinylchloride or polyfurfurylalcohol can give the desired alteration.

EXPERIMENTAL

A– Material

Hard pitch (HP) and Petroleum coke (PC) were obtained from L.T.D. Co. (England).

As modifier, polyfurfurylacohol (PA) was selected since it was thought that this polymer can have pore blocking action and filling property of the crevices which are inevitable during baking. This polymer was prepared in the laboratory using acid catalyst[4].

The other synthetic polymer selected was polyvinylchloride (PVC). This polymer too passes through a plastic state before melting and gives graphitising carbon by further heating[5]. On the other hand, in road asphalting PVC is successfully used as gravel binder modifier. Considering these properties PVC was chosen as binder modifier and bought from the market with trade name Geon 113.

B– Method

Carbonisation was performed in the same apparatus whose pertinent detalis were discussed elswhere[5]. The samples, after being prepared were situated in the homogeneous heating zone of the furnace in quartz floats.

70 g of PC, ground to 200 mesh and 30 g of HP, heated to 150 °C were mixed thoroughly into a paste. 25 g of this paste was put in a quartz float by pressing slightly with a spatula. The proportion of the synthetic polymer was 15 %. The samples prepared in this way were put in furnace. In order to purge the system nitrogen gas at a flow rate of 400 ml. min^{-1} was used for one hour. Then keeping the same nitrogen flow rate, the furnace was heated at a rate of 15 C°. min^{-1} up to carbonisation temperature and the sample was hold at this temperature for six hours. The furnace was eventually cooled under the same nitrogen flowrate. The carbons produced in this way were ground to 20 mesh particle size and were stored in a dessicator under nitrogen atmosphere.

Adsorption studies were carried out in a conventional volumetric adsorption apparatus at – 196 °C. Before the adsorption experiments, samples were subjected to outgassing overnight at 125 °C.

The apparent densities were determined in a specially made picnometer that can be joined to the vacuum line, by using carbon tetrachloride and mercury as displacement fluids.

Results and Discussion

The weight losses, apparent densities and specific surface areas of the samples obtained under explained conditions, were determined experimentally. Using these experimental data monolayer capacity

(Vm ml. g^{-1}), pore volumes at saturation (Vs ml. g^{-1}) and total pore volumes (V_T ml. g^{-1}) were calculated.

At 500 °C while the weight loss of HP was 35 %, these were 10.9 %, 14.2 %, and 12.6 % for the mixture of HP–PC, HP–PVC–PC and HP–PFA–PC respectively. At higher temperatures the weight losses were increased. Thus at 1100 °C weight losses of HP, HP–PC, HP–PVC–PC and HP–PFA–PC were 44.8 %, 14.92 %, 22,87 %, and 19.01 % respectively.

The apparent densities determined by carbon tetrachloride and by mercury as displacement liquid were increased when the temperature was increased. It was also found that the apparent densities of the carbons of HP–PC and HP–PVC–PC mixtures determined by carbon tetrachloride as displacement liquid were very close to that of graphite.

The increase of the ratio of specific surface areas of the different samples obtained at various temperatures were found especially noticeable. In the carbonisation of the HP on its own, increasing the temperature from 500 °C to 1100 °C was caused the surface area to increase from 0.1 $m^2. g^{-1}$ to 1.0 $m^2. g^{-1}$, that is doubling the temperature causes ten-fold specific surface area increase. The carbons obtained from the mixture of HP–PC show the highest increase on the ratios of the surface areas at a specified temperature. The surface area of the sample obtained by the carbonisation of HP–PC mixture, was larger than those of the HP carbonisation products. The values measured at 500 °C was 4.8 $m^2. g^{-1}$ and at 1100 °C was 89.3 $m^2. g^{-1}$ That means introducing petroleum coke increased the surface area nearly 20 times The experiments showed also that addition of PVC and PFA into the mixture caused only 4 and 1.5 fold increase on the surface area respectively.

For all samples prepared, except those containing PFA a decrease on the mean pore radius ($\bar{r}$) was found. However, the mean pore radius

did not show significant alteration with temperature. For the samples prepared at 500 °C and 1100 °C the calculated ($\bar{r}$) values were 10.76 Å and 10.52 Å respectively.

According to BET classification, basically all adsorption isotherms were Type I and no hysteresis loop was observed. The results obtained are tabulated in Table–I and adsorption isotherms are presented in Figures from 1 to 3.

Heating is the reason of the plastic state and gas evolution from the HP. In the 400–450 °C temperature range plastic state is conspicious. On the other hand, evolution of the gas is the sign of some chemical decompositions[6]. The viscosity decreases due to the increase of the thermal mobility when the temperature range mentioned above is reached. At the same time, chemical decomposition may cause the occurence of the compounds with complex structure which in turn may increase the viscosity. Theoretically it can be assumed that introducing the synthetic polymers may stop the fluctuation of the viscosity due to the very high molecular weight. As it can be easily accepted that stabilisation of the viscosity is an important factor in preventing the segregation and providing sufficient wetting of the particles. The occurence of the volatiles takes place as a result of the chemical changes during the carbonisation. These gaseous products leave void spaces and by the help of the ultrafine micropores, reach to the surface of the mass and diffuse to the atmosphere. Higher surface area, in the electrode mixtures containing only HP as binder, than the synthetic polymer containing mixtures can be attributed to the lower viscosities envisaged in the unmodified mixtures which permits the transport of the gas molecules produced by the chemical reactions while the carbonisation in progress, thus resulting the pore structure development at high levels.

While no sharp changes of physical states can be observed in the mixture of the carbonisation of the HP–PFA–PC, conspicious state

changes are observed in the HP–PC and HP–PVC–PC mixtures. Another observation was 0.3–2 mm diameter spheres in the melt of HP–PVC–PC mixture. The probable reason for the agglomeration of the filler particles may be the surface tension of the fraction of low molecular weight compounds in liquid phase. When the carbonisation was completed this appearance did not change. The higher weight loss of the HP–PVC–PC than HP–PFA–PC mixture can be explained with the evolution of the gaseous compounds which is facilitated by the low viscosity and the agglomeration already mentioned.

The highest BET surface area was obtained from the carbon produced from HP–PC mixture. It is already well known that the surface area increases or decreases by the partial oxydation which takes place in the active centers of the surface during heat treatment under working conditions. The concentration of the relative molar active centers was found to be very high in the heat treatment of the HP[7]. It is assumed that introduction of the synthetic polymer not only decreases the active site concentration but also causes blocking hence prevents the development of the micropores. thus the surface area is reduced. The surface area of the HP–PFA–PC carbon was found to be the lowest amongst other carbons prepared. This mixture does not melt when it is heated but has a metaplast state which leads to the conclusion that there has to be no porosity at all. However, although it is small, measurable size of the surface area is a definite sign of the porosity. Hence, considering this experimental fact, one can draw the conculsion that metaplast formation can not stop the porosity development. In other words, metaplast state, instead of preventing the occurence of the labile carbon atoms, it helps for the microporosity to develop up to a certain extend. As the surface area of the PVC containing carbon is higher than PFA containing carbon, metaplast and following melting states provide a suitable media for the micropore structure to develop.

As it was stated before, in HP and HP–PC carbons the surface areas show 10 and 20 times of increase respectively by increasing the temperature from 500 °C to 1100 °C. In modified mixture carbons this increase is lower. In the case of PVC modified carbon, the surface area has increased 5 times, corresponding value for the PFA containing carbon is only 1.5 (See Table–I.). These increases can be attributed to the secondary gas evolution which is responsible of some crevices to appear during the baking process of the carbon artifact at high temperature and to the destruction of the coke structure by heat treatment.

The end of the carbonisation can be determined from the solidification of the mass and stabilisation of the bubble structure of the liquid state. Depending on working conditions and on properties of the raw materials, further heat treatment causes the evolution of some gases, mainly hydrogen and in lesser quantities carbon monoxide and carbon dioxide. Thus the surface areas increase and pore radius decreases. (See Table–I.) At the temperatures higher than 1000 °C, reorientation of the carbon atoms take place to form a regular and closed crystal structure. The experimental evidences for this conclusion are the reduction of the mean pore radius and the gradual increase of the apparent densities (See Table–I.).

Table–I shows that 15 % of the PVC reduces the surface area of the HP–PC mixture by 40 %. The addition of the PFA in the same proportion causes some dercease on the surface area which is about 85 %. In the carbonisation of some polymers a plastic state is observed. At this stage free radicals or radical chain fragments also occur[8]. After plastic state has been passed, the mass turns into a state that corresponds to the metaplast phase which is envisaged during the carbonisation of coal. All these changes are accompanied by the exclusion of the some small molecules from the chain such as hydrogen, hydrogenchloride etc. [9,10] Hence micropore structure develops. The results presented in

Table–I shows that pore blocking capacity of the PFA is higher than PVC. The possible reason for that can be different carbonisation characteristics of the PVC and PFA. In differential thermal analysis PVC gives an endothermic peak at 300 °C, PFA on the other hand produces an exothermic peak starting at 370 °C and reaching to the completion at 650 °C[11]. Lamond et. al. observed that at 530 °C fusing takes place in the thermal decomposition of PFA[12]. Considering these two reports one can say that up to acertain extend PFA may stay in fluid state while PVC carbonises and stabilises its structure. Thus it is natural for the PFA to have higher pore blocking capacity at relatively high temperatures. If this is the case the mean pore radius of the PFA containing sample has to be smaller than PVC modified carbon. However, experimental results contradict this conclusion. (See Table - I) If it is remembered that; PVC produces graphitising type carbon and under the working conditions of this study, graphitisation can proceed. Hence the contradicition mentioned can find an explanation.

Investigation of the figures 1, 2 and 3 show that, the slopes of the linear portions of the nitrogen adsorption isotherms of the PFA containing samples are steeper than the others and they stay paralel even after the heat treatment at 1100°C. According to Brunauer, Emmet and Teller[13] this observation can be interpreted as the sign of homogeneous pore structure. The observation also explains the equality of the mean pore radius found for the samples containing PFA (See Table–I).

The third column of the Table–I presents the apparent densities. and in the sixth column specific total pore volumes which were calculated from the difference between the specific volumes given by the mercury and carbon tetrachloride, are tabulated. Assuming that the mercury at atmospheric pressure will not enter the pores of diameter less than 7μ the quantity $1/d_{Hg}$ is almost equal to the lump volume of the adsor-

Table I: Surface properties of different Carbon binder mixtures obtanied at various temperatures.

Carbonisation temp., °C.	Wieght loss, %	Apparent density, g. cm^{-3}		BET surface area, m^2. g^{-1}	Monolayer capacity V_m, ml.g^{-1}	Pore volume from liquid density V_T, ml. g^{-1}	Pore volume at saturaiton, V_S, ml. g^{-1}	Pore diameter $\bar{r}$, Å
		CCl_4	Hg					
				HP				
500	35.0	1.38	1.15	0.1	0.2	93.2	1.0	339.0
700	42.0	1.48	1.29	0.4	1.0	63.9	1.9	153.9
900	44.0	1.70	1.32	0.7	1.4	108.9	3.0	133.7
1100	44.8	1.83	1.37	1.0	2.2	117.9	3.5	108.9
				HP – PC				
500	10.9	1.79	1.74	4.8	1.0	10.3	2.2	23.5
700	12.6	1.89	1.70	13.9	3.2	38.0	4.2	9.4
900	93.8	1.92	1.65	32.0	6.0	54.8	8.2	7.9
1100	14.9	2.01	1.60	89.3	19.9	81.9	16.8	5.9

HP – PVC – PC

500	14.2	1.82	1.78	12.8	3.5	7.9	6.0	14.6
700	20.6	1.83	1.78	14.9	4.0	9.8	6.2	12.9
900	21.9	1.88	1.76	22.4	5.2	23.3	8.6	12.0
1100	22.8	2.00	1.82	49.4	11.8	31.8	14.3	9.1

HP – PFA – PC

500	12.6	1.80	1.77	8.9	1.6	6.06	3.1	10.8
700	14.5	1.83	1.79	9.6	1.7	7.85	2.9	9.7
900	15.78	1.85	1.79	10.0	1.9	11.65	3.4	10.6
1100	19.01	1.89	1.82	13.3	6.2	13.08	4.5	10.5

bent, that is, the volume of the solid material. Carbon tetrachloride on the other hand will enter all pores except those having a width less than its molecular diameter[14]. Thus the difference $1/d_{Hg} - 1/dc.cl_4$ should practically equal to the pore volume of the solid. As it can be seen from the Table–I, V_T values of every individual sample increase with the increasing temperature, which is quite natural if the surface area values are examined that are given in the same table. Introduction of PVC and PFA into mixture reduces V_T values from 117 ml. g^{-1} in HP down to 31. 80 ml. g^{-1} and 13.08 ml. g^{-1} respectively after 1100 °C carbonisation. This is a strong evidence of the pore blocking action of synthetic polymers selected.

The last column of the Table–I represents mean pore radius calculated from the specific surface area and from the pore volume at saturation[15]. Rising the temperature decreases mean pore radius. This observation can be taken as an evidence of some alterations of the pore structure. The possible reason of the decrease can be the pore blocking action of the modifiers along with narrowing of the orifices of the pores by heat and total closure of some cavities.[16,17]

In conclusion; addition of the PVC and PFA decreases microporosity considerably which in turn, it is believed will reduce the consumption of the electrodes. The amount of synthetic polymers introduced in the mixture was chosen arbitrarily and all the samples were prepared in laboratory scale. The effects of the alteration of the quantity of synthehetic polymers and examining the increase of the sample size are two important questions open to further studies.

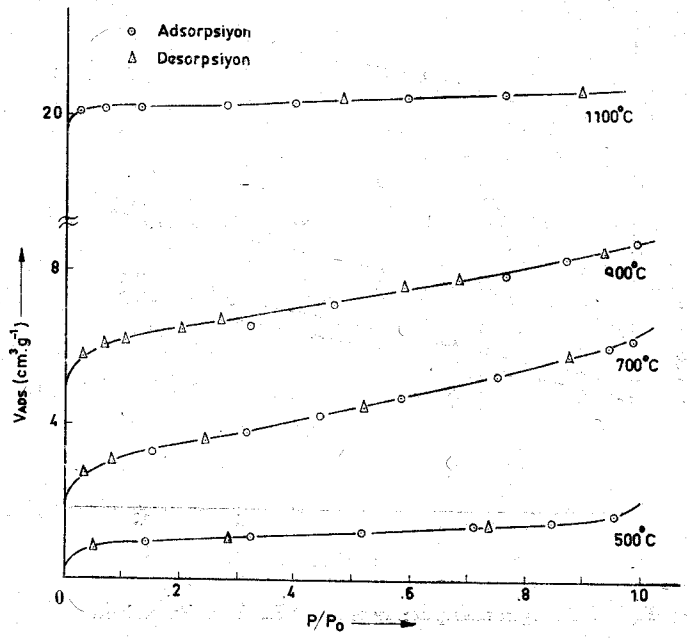

Fig – 1: Nitrogen adsorption isotherms of HP–PC carbons.

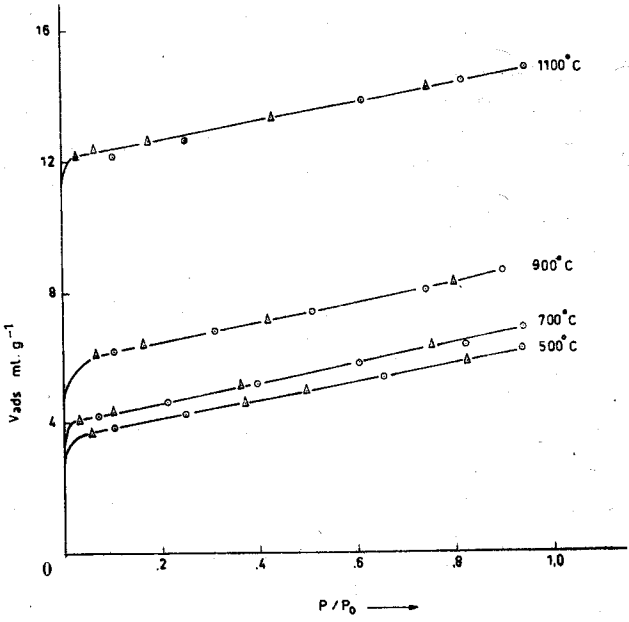

Fig – 2: Nitrogen adsorption isoterms of HP–PVC–PC carbons.

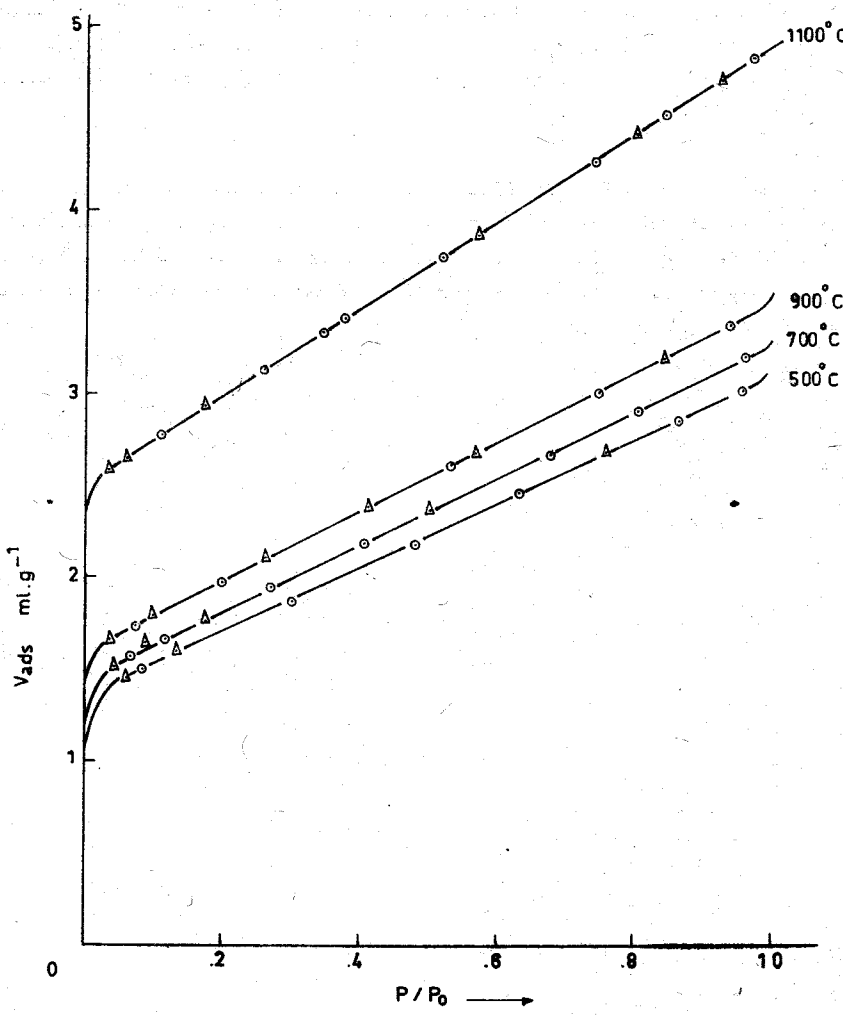

Fig – 3: Nitrogen adsorption isotherms HP–PFA–PC electrode carbon

ÖZET

Elektrokimyasal teknolojide kullanılan karbon elektrot üretiminde zift, ucuz ve sağlanmamasının kolay oluşu nedeniyle geniş ölçüde kullanılır. Ancak, bu maddeden elde edilen karbon, elektrot sarfiyatını ve çalışmasını doğrudan doğruya etkileyen oldukça geniş bir yüzey alanına sahiptir.

Bu çalışmada polivinil klorür ve polifurfuril alkol kullanarak zift karbonunun yüzey alanının düşürülüp düşürülemiyeceği araştırılmıştır. Elde edilen sonuçlara göre % 15 oranında polifurfuril alkol ilâvesi yüzey alanını, 89,5 $m^2 . g^{-1}$ den, ki bu değer petrol koku zift karışımı karbonu için bulunmuştur. 13,3 $m^2 . g^{-1}$ değerine kadar düşürmektedir. Polifurfuril alkol ilâvesi ile aynı zamanda gözenekliliğin de homojen olarak geliştiği saptanmıştır.

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