Effects of carbon pretreatment for oxygen reduction in alkaline electrolyte

Massoud Pirjamali, Yohannes Kiros[*]

Chemical Reaction Engineering, Department of Chemical Engineering and Technology, KTH,
Royal Institute of Technology, S-100 44 Stockholm, Sweden

Abstract

The effects of different media on carbon pretreatments for oxygen reduction in alkaline electrolyte without application of active electrocatalysts were examined. Low surface area Vulcan XC-72 and high surface area Ketjenblack EC-300 were subjected to aqueous acid (flouric or formic), gaseous (H_2, N_2 or CO_2) and thermal treatments at 600 or 900 °C. Though non-scrubbed air was used, as a result of which carbonate build-up was high and peroxide concentration increased due to the electrode reaction, some of the electrodes resulted in life-tests of more than 2000 h at 65 °C, 6 M KOH with a constant load of 50 mA cm^{-2} and intermittent polarisations at higher current densities. BET-surface areas and pH changes of more than 60% and weight losses of up to 15% of the carbon blacks were observed after the pretreatment steps. Electrochemical characterisation of the carbons showed that pretreatment steps of the carbon blacks have a significant effect on the long-term stability and activity of the gas diffusion electrodes in alkaline electrolyte. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Low and medium temperature fuel cells, electrolysers, double-layer capacitors and Li-ion batteries use carbons as catalyst supports or as active materials for energy storage and conversion. Carbon materials are preferred due to their high electrical conductivity, low cost, high surface area, porosity, formability and their chemical and electrochemical resistivity. Nitrogen-incorporated films, polyacrylnitrile based carbon fibres, nanocomposites and carbons prepared by mechanical and thermal treatment procedures have been extensively used due to their superior cycle performance and high capacity per unit mass [1–6]. However, for long-term operation, performance and stabilisation of the three phase boundary of the gas diffusion electrodes, especially in alkaline electrolytes, where the carbon material serves both as a support and/or catalyst in the overall electrochemical reaction scheme, pretreatment of the carbon is of prime importance. Furthermore, pretreatments are supposed to increase corrosion resistance in the temperature range and electrolyte concentration of interest for operating primary/secondary batteries and fuel cells.

Carbon materials, prior to their impregnation with the active catalysts of oxygen reduction or hydrogen oxidation, are pretreated to obtain desired changes in their structures. Thermal treatment of carbons is usually conducted at temperatures ranging from 400 to 2700 °C in the presence of gases and in the presence or absence of organic or inorganic additives to cause a "burn-off" and thereby alter the physicochemical properties. Effects similar to the thermal and gas-phase reactions are also achieved by surface treatments with aqueous solutions of HNO_3, dichromate in acids and HF, H_3PO_3, H_2SO_4, etc. [7–14]. These thermal, gaseous or aqueous pretreatments often result in the exposure of fresh edge planes and microparticles, direct intercalation or reintroduction and/or removal of oxygen or hydrogen containing complexes and inorganic compounds, change in specific surface areas, lattice parameters, crystallite sizes, particle size, resistivity and wettability, etc. of the precursor. The reactivity of carbon is mostly dependent on the chemical structure of the carbon precursor, accessibility of the surface areas to the reactants and the heat treatment temperature (HTT). Ross et al. [15] reported on the corrosion behaviour of various types of furnace blacks with differing surface areas, when after undergoing heat treatments at 2700 °C, showed chemical resistances by factors of 2.5–20 for the oxygen evolution reaction (OER) in 30% KOH. Appleby

---

et al. [16] have also studied 47 different carbons and graphites with various physicochemical properties and assessed the kinetics for the oxygen reduction reaction (ORR) on ultra-thin electrodes. Tafel slopes as a function of the surface properties of the carbons were found to vary from 40 to 60 mV per decade. The role of acid, base and neutral properties of the carbons are also important for the application of electrocatalysts [17,18] in order to increase or decrease the dispersion and/or sintering rates both during the heat treatment and the subsequent electrochemical reactions. Therefore, studies concerned with activation of carbon using gas or liquid-phase reactions at high temperatures for the assessments of long-term stability and activity, especially in alkaline electrolytes are of special interest.

In a previous report [19], we have shown that optimum conditions for the ORR of a carbon and catalyst mixture lied in the range of 80–100 $m^2 g^{-1}$. Reports on carbon–catalyst mixtures for fuel cells applications, heat-treated at high temperatures and in the presence of gases are primarily concerned with reduction of the inorganic or organic compounds and determination of the chemical and physical structures of the catalysts on carbon. The interactions of carbon with the catalyst and/or the synergetic effect of both, however could give different interpretations of the results. In this study, porous carbon based gas diffusion electrodes for the ORR without catalysts were prepared from two different kinds of carbon blacks, which have undergone different thermal and/or chemical and physical (gaseous) treatments prior to long-term electrochemical testing. Changes in surface areas, weight loss, chemical properties and pH have been recorded and alluded in order to substantiate how pretreatments and changes of the physicochemical characteristics of the carbons affect the electrochemical stability and activity of gas diffusion electrodes. The scope of the work on 40 different samples and two reference precursors, enables us to look into factors influencing long-term activity of pretreated carbons and their eventual application not only as a support for the electrocatalyst but also as active material for enhancement of the overall performance and stability in alkaline electrolytes.

2. Experimental

Carbon blacks, Vulcan XC-72 and Ketjenblack EC-300 with the characteristics shown in Table 1, obtained from the manufacturers' data, were subjected to different treatment procedures. The carbon materials were treated by aqueous solutions of >98% formic or 38% hydrofluoric acids, flowing gases of nitrogen or 5% carbon dioxide or 10% hydrogen in nitrogen at temperatures of either 600 or 900 °C. The acidic immersions of carbons were performed at room temperature, allowed to settle and react for 3 h, filtered and rinsed with deionized water and dried at 70 °C. The carbon materials were placed in a crucible in a quartz tube furnace for 5 h so that the gas–solid phase reactions could take place at respective temperatures. The gas and heat-treated samples were then kept in a water-cooled zone of the furnace in a nitrogen atmosphere until the temperature had come down to ambient temperature.

Single-layer gas diffusion electrodes were prepared using the pretreated samples, comprising of 65% carbon and 35% PTFE powder. Both materials were mixed and homogenised in a mixer after which a hydrocarbon solvent was added to obtain a dough to be rolled into a thickness of 0.7 mm on a nickel wire screen (100 mesh), which provided the function of a current collector and structural support. The electrode was then pressed (140 kg cm^{-2}), dried for 2 h at 60 °C and was sintered at 300 °C in a flow of nitrogen for 1 h. Nickel wire was spot-welded to the electrode and rectangular specimen of 4 cm^2 were assembled in a half-cell configuration for the electrochemical test and evaluation. The electrode was then immersed in 6 M KOH with a nickel wire mesh serving as a counter electrode. Details of the preparation method of the electrodes and the schematic of the electrochemical cell were reported previously [19]. Non-scrubbed air was introduced at the rear side of the electrode, where the temperature was kept at 65 °C using a thermostated water bath. A Hg/HgO reference electrode with the same electrolyte concentration and a Luggin capillary in contact with the electrode was used to read the potential variations in the long-term comparative studies of the various types of porous gas diffusion electrodes. The durability tests for all gas diffusion electrodes were terminated, when the electrode potential reached at an end potential of −350 mV.

Surface areas of the carbons were measured using single-point Micromeritics Flowsorb II. The nitrogen adsorption isotherms were carried out in degassed samples at liquid nitrogen temperature (−196 °C). A standard test procedure by the American Society for Testing Materials (ASTM) was used to assess the pH of the carbon blacks. The pH values were obtained by mixing 1 g of the sample with a magnetic stirrer in a 25 ml preboiled distilled water and further boiling it for 3 min. The hot slurry was then filtered, sealed from any contact with atmospheric air, allowed to cool down to room temperature and finally analysed after calibration of the pH meter with standard buffer solutions. The carbonate

Table 1
Physicochemical characteristics of the carbon blacks

Type of carbon	Surface area ($m^2 g^{-1}$)	Average particle size (nm)	Volatile content (%)	Supplier
Vulcan XC-72	254	30	1.5	Cabot
Ketjenblack EC	800	30	0.6	AKZO chemie

concentration in the long-run tests due to the reaction of hydroxide with carbon dioxide was also analysed using the gravimetric method on aliquots withdrawn from the electrolyte. Potassium carbonate was treated by barium chloride and the barium carbonate precipitate was used to determine the amount of carbonate in the electrolyte according to the following reaction.

$$BaCl_2(l) + K_2CO_3(l) \rightarrow BaCO_3(s) + 2KCl \qquad (1)$$

The quantitative chemical composition of the carbon samples both before and after treatment was analysed using energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1. Weight loss

The weight losses of the carbon blacks after chemical and heat treatments are shown in Table 2. The overall weight losses are not significant for Ketjenblack EC, irrespective of the acidic or gaseous media or at lower or higher temperatures. Gas treatment with carbon dioxide, however shows changes of up to 4.2% at 900 °C, showing that carbon dioxide has only a minor oxidising character on the carbon black structure. More weight changes were obtained for

Table 2
Weight loss, pH changes and electrochemical tests after the chemical and thermal treatments

Sample name	Treatment conditions			Characterization				
	Acid	Gas	Temperature (°C)	Loss (wt.%)	pH	BET ($m^2\,g^{-1}$)	E (mV vs. Hg/HgO) at 50 mA cm^{-2}	Cell test (h)
V 0	–	–	–	–	6.85	223.77	−240	744
V600H	–	H_2	600	2.2	8.11	232.57	−225	864
V600N	–	N_2	600	1.9	7.50	230.16	−230	672
V600C	–	CO_2	600	2	7.80	227.04	−232	640
V900H	–	H_2	900	2.5	7.96	236.68	−215	552
V900N	–	N_2	900	3	7.47	239.89	−219	576
V900C	–	CO_2	900	14.8	7.60	364.75	−209	1152
VM 0	Formic	–	–	–	5.74	226.69	−255	864
VM600H	Formic	H_2	600	1.7	8.09	236.73	−302	576
VM600N	Formic	N_2	600	1.4	7.69	228.91	−260	840
VM600C	Formic	CO_2	600	1.4	7.95	228.51	−250	1008
VM900H	Formic	H_2	900	4.7	8.01	255.61	−212	1704
VM900N	Formic	N_2	900	4.8	7.71	270.51	−213	1056
VM900C	Formic	CO_2	900	7	7.84	304.47	−205	2784
VF 0	Flouric	–	–	–	4.97	218.57	−279	576
VF600H	Flouric	H_2	600	1.8	8.11	230.89	−222	840
VF600N	Flouric	N_2	600	1.5	7.66	229.37	−224	672
VF600C	Flouric	CO_2	600	1.9	7.74	233.09	−202	912
VF900H	Flouric	H_2	900	5.4	8.09	277.83	−240	624
VF900N	Flouric	N_2	900	5.5	7.56	268.22	−200	1728
VF900C	Flouric	CO_2	900	8.7	7.68	288.25	−211	2496
K 0	–	–	–	–	5.82	752.56	−245	816
K600H	–	H_2	600	0.6	7.32	755.60	−224	1680
K600N	–	N_2	600	0.7	7.34	750.85	−233	1440
K600C	–	CO_2	600	1	8.05	750.35	−247	1512
K900H	–	H_2	900	2	7.06	766.54	−227	960
K900N	–	N_2	900	1.8	7.31	912.65	−209	1920
K900C	–	CO_2	900	3	8.05	805.15	−206	1872
KM 0	Formic	–	–	–	5.95	731.37	−233	768
KM600H	Formic	H_2	600	1.3	7.64	762.75	−240	1176
KM600N	Formic	N_2	600	1.6	7.48	763.50	−243	1320
KM600C	Formic	CO_2	600	1.0	7.81	748.87	−216	1368
KM900H	Formic	H_2	900	1.6	7.28	783.42	−218	2088
KM900N	Formic	N_2	900	1.5	7.46	869.90	−216	2712
KM900C	Formic	CO_2	900	4	8.15	799.24	−206	2112
KF 0	Flouric	–	–	–	5.28	746.19	−294	720
KF600H	Flouric	H_2	600	1.5	7.45	751.12	−232	952
KF600N	Flouric	N_2	600	1.8	7.38	756.33	−220	1048
KF600C	Flouric	CO_2	600	1.4	7.74	759.33	−235	1180
KF900H	Flouric	H_2	900	1.6	7.26	817.13	−220	1504
KF900N	Flouric	N_2	900	1.8	7.55	829.27	−206	1692
KF900C	Flouric	CO_2	900	4.2	8.05	781.79	−209	1132

V—Vulcan XC-72, K—Ketjenblack EC, 0—as received or thermally untreated, F—fluoric acid, M—formic acid, H, N and C—Hydrogen, nitrogen and carbon dioxide gases, 600 and 900 °C heat treatment temperatures.

Table 3
Quantitative analyses of sulphur composition by EDS over selected Vulcan XC-72 samples

Type of carbon and treatment	Elemental (%)	Atomic (%)
V0	0.33	0.12
VM0	0.16	0.06
VF0	0.10	0.04
V900H	0.10	0.04
V900N	0.14	0.05
V900C	0.10	0.04
K0	0.10	0.04

V—Vulcan XC-72, K—Ketjenblack EC, 0—as received or thermally untreated, F–fluoric acid, M–formic acid, H, N and C–Hydrogen, nitrogen and carbon dioxide gases and 900 °C or no heat treatment temperature.

Vulcan XC-72 at high temperature treatment. The "burn-off" or "activation" is more pronounced with carbon dioxide as it constitutes a mild oxidation agent compared to the reducing or inert atmosphere of hydrogen and nitrogen, respectively. These changes might be ascribed to the loss of functional groups, such as surface oxides of Vulcan XC-72 and sulphur and sulphuric compounds over selected samples as depicted in Table 3, analysed by EDS. EDS analyses over Ketjenblack EC, except for the as-received are not reported in the table as this product primarily didn't contain any detectable amount of sulphur in the range of the analytical instrument. As heat-treatment of carbons at very high temperatures reduces the sulphur content, the immersion of the carbons in the acids followed by water rinsing results in substantial decrease of the sulphur amount. Furthermore, the reactivity of the carbons might also depend on the process parameters such as temperature, gasifying agent, flow rate, residence time, and pressure as well as on carbon properties such as porosity, impurities and active site distribution and concentration on the surface [20,21].

3.2. pH values

The pH values of the aqueous slurries provides an indication of the surface functional groups of the carbon blacks and is equivalent to the point of zero charge of the materials [22,23]. The pH values of the slurries of carbon blacks illustrated in Table 2 varied a great deal from a slightly acidic for the untreated or acid-treated samples to a higher value of basicity. The acid-base properties of the carbon blacks emanates from either the Brönsted acids or Lewis bases, with the equilibrium reactions of the carboxylic groups or the so-called *p*-sites of the carbon as sites on the carbon surface with maximum density of delocalised electrons [24]. The *pH* < 7, thus tabulated alongside the acid treated carbons and mainly of the precursor materials can be ascribed to the protonation reaction, while the higher pH of those treated with gases and temperatures are favoured by the reaction of the basal plane of Cp to bind the protons to its *p*-structure [25] as an explanation to these discrepancies in the pH values.

Studies on furnace blacks have shown that carboxylic and lactone groups begin to evolve at temperatures as low as 250 °C, while the quinone and phenol groups are liberated at temperatures between 500 and 900 °C [26]. Higher pH values were obtained for Vulcan XC-72 both at 600 and 900 °C in the presence of hydrogen. Correspondingly increase in pH was obtained for Ketjenblack EC, when exposed to carbon dioxide at both temperatures of heat treatments. Heat treatment of the carbon blacks at higher temperatures proceeds with the decomposition of the acidic surface oxygen groups to CO_2 and CO and replacement with other surface complexes. Thus, the increase in pH is mainly due to changes in surface properties of the carbons, such as surface area, porosity, concentration of surface groups and capability of the these groups to react with specific gases. These parameters in turn lead to the dissociation of the heteroatoms (sulphur, oxygen, inorganic impurities) and slight or complete replacement of the edge groups by C–H bonds and other complexes [27,28].

3.3. BET-surface areas

Heat treatment results in changes of the surface areas, pore size distributions and chemical properties of carbon blacks. Although surface areas can be measured reliably with as little as 0.1 m^2 of total surface or as much as 280 m^2, the sample masses were weighed after appropriate vacuum outgassing at 200 °C for 2 h so as to lie within the accuracy/reproducibility of the measuring equipment of 15 to 25 m^2. Thus, repeated tests over nine randomly selected samples showed an accuracy of ±0.5% and a deviation of less than 1%. At 600 °C, irrespective of the gaseous treatments, the surface areas of the carbon blacks have not shown any substantial increase compared to the original or acid-treated samples as shown in Table 2. However, upon heat treatment at 900 °C in CO_2 for Vulcan XC-72 and in N_2 for Ketjenblack EC, the surface areas show a significant increase of between 11 and 60% compared to the as-received carbons. Gas treatments in CO_2 and N_2 at 900 °C without any further addition of acids show a profound increase for respective carbons, implying that the changes in surface areas are due to the opening up of the porosity and release of internal surface area. Thus, the BET-surface area increase is a function of the temperature, type of gas and chemical treatment as well as the structure and origin of the carbon blacks.

3.4. Electrochemical testing

Carbon blacks, are normally used in electrochemical systems, especially in alkaline electrolytes either as conductive supports or active materials for oxygen reduction and hydrogen peroxide formation as shown in reaction (2) with a potential versus the normal hydrogen electrode (NHE) at a standard state.

$$O_2 + H_2O + 2e^- \leftrightarrow HO_2^- + OH^- \quad (E_0 = -0.065 \, \text{V})$$

$$(2)$$
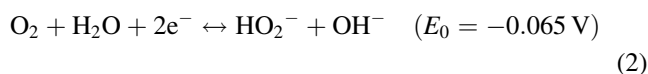
The performances of the non-catalysed carbon blacks, that have undergone heat and chemical treatments, are shown in Table 2. The data shows among the best performances recorded for the different electrodes at a constant current density of 50 mA cm^{-2}. The electrodes were polarised at high current densities twice at the start and once a week at the end of the experiment in 6 M KOH and at 65 °C with a constant supply of air containing the small concentrations of CO_2 (~360 ppm). Although activity and mode of pretreatment are not correlated throughout the results in the electrochemical testing, high temperature treatment at 900 °C has predominantly shown an increased activity towards the ORR compared to HTT at 600 °C. This increase in performance can be ascribed to the increase in BET-surface areas and in the availability of the microporosity of the carbon as well as devolatilization of the oxygen surface groups, leading to a higher electroconductivity [29]. Studies by Appleby et al. [16] on different carbon materials on the kinetics of oxygen reduction, have shown that due to the high accessibility of the carbon black surfaces, the change in mechanism (lower Tafel plots) is a function of the surface areas.

Long-term stability tests of the electrodes are also shown adjacent to the performance values in Table 2. Many of the electrodes have shown a characteristic durability test of more than 1000 h, some exceeding 2000 h of electrochemical operation. Electrodes, prepared from high surface area samples pretreated either by CO_2 for Vulcan XC-72 or by N_2 for Ketjenblack EC, have shown superior life-tests. Generally, the effect of formic acid treatment has shown a more profound effect in the stability tests of the electrodes than the simple gas or fluoric acid treatment. This may be due to the strong reducing properties and its aldehyde and carboxylic acid properties. The failure of some of the electrodes, which were compared at the end potential of −350 mV, has to do with how fast the electrolyte penetration or wettability takes place in the porous structure of the electrodes. This was observed when carbonate was formed at the gas-side totally plugging the flow of air into the electrode. Analyses of carbonate formation in the electrolyte after 1176 and 1272 h, have shown concentrations of 0.655 and 0.665 M K_2CO_3, respectively. Besides the carbonate build-up in the electrolyte, precipitation takes place in the microporous structures of the carbon electrodes changing the non-wettability of the electrodes. Furthermore, the reaction of CO_2 with the electrolyte leads to the depletion of OH^- ions according to the reaction $CO_2 + 2OH^- \leftrightarrow CO_3^{2-} + H_2O$. This step in turn leads to the increase of the electrolyte viscosity affecting the diffusion rate with subsequent decline in the limiting current as well as interference with the electrode kinetics. Studies on five randomly selected electrodes were carried out in order to assess the reproducibility of the electrodes both in performances and durability. The performances were found to lie within ± 9 mV, whereas the stability was within ±35 h.

Factors influencing the long-term stability of carbon electrodes to be used in alkaline electrolytes, are the surface areas and mode of physical, chemical and thermal treatments.

The increase in overpotentials for the ORR is a function of the wetting properties of the carbon materials, carbonate formation and increase of the peroxide concentration. The differences, thus shown among the electrodes may be attributed to the porosity, which as a result of the reaction are filled with electrolyte, leading to slow deterioration of the electrodes. The three-phase boundary between liquid/solid/gas is altered leading to eventual "drowning or flooding" of the solid phase and thus, blocking the flow of the reactant gas through the network of gas channels and thereby reduces the effective area leading to poor performance and stability [30]. The wetting properties of the electrodes can be effectively hindered by highly wet-proofing a gas diffusion layer or employing a backing (teflon) layer, so that electrolyte leakage or droplets on the gas-side are not formed. Carbon dioxide removal from the mainstream of air is also crucial for both the activity and stability of the electrodes. Thus, effective adsorbents for CO_2 are of great importance in order to avoid the consequences of carbonate formation, resulting in the wettability of the electrode. Furthermore, the reduction of HO_2^- (reaction 2) on ash-free or without electrocatalysts is slow, where at substantial current densities peroxide concentration in the internal pores is increased [31], resulting in the decay or degradation of the activity and stability. Admixture of peroxide ion reduction or decomposition catalysts (e.g. Pt, macrocycles, perovskites, etc.), which dispersed on high area carbon support and/or electrocatalyst should enhance both the service life and performance of gas diffusion electrodes.

4. Conclusion

The activity and durability tests of carbon-based gas diffusion electrodes strongly depend on the mode of thermal, chemical and physical pretreatment of the carbon blacks. The pretreatment steps in turn influence the surface and physicochemical properties of the carbons to be selectively applied for the ORR in alkaline electrolyte. The ageing rate could be ascribed to the disruption of the three phase boundary, when electrolyte penetration and inaccessibility of oxygen in the porous system of the electrodes become dominant. Furthermore, carbonate precipitation in the porous system significantly enhances the "flooding" of the electrode and suppresses the hydroxide concentration as well as interferes with the electrode kinetics, effect on the durability and activity of gas diffusion electrodes. Based on the results obtained in this study, the following conclusions could be deduced from the effects of pretreatment on the physicochemical changes of the carbon black materials as well as on their electrochemical activity and stability for the ORR.

- High weight loss of the carbon blacks are observed when they are pretreated at high temperatures and in the presence of CO_2, which might be ascribed to the loss of the volatile or oxygen containing groups. The more the volatile content, the larger is the loss of weight.

- High pH changes are encountered for all samples of Vulcan XC-72, when heat-treated at both 600 and 900 °C in the presence of hydrogen gas, while the same effect is observed at both temperatures when samples of Ketjenblack EC are treated with CO_2.
- Increased BET-surface areas have been measured for Vulcan XC-72 when heat-treated at 900 °C in the presence of CO_2, while the same observations were achieved for Ketjenblack EC at the same temperature but in nitrogen atmosphere.
- Although no clear distinction is to be observed on the relationship between the electrochemical activity towards ORR and the characterisations of the carbon blacks, the potentials at 50 mA cm^{-2} show that increased temperature treatment has more significant effect on better electrode performances than low temperature treatments.
- High temperature treatment and high BET-surface area carbon blacks have shown increased stability for the gas-diffusion electrodes in the alkaline media. An overall increase in stability could be noted for carbon blacks treated with formic acid than the corresponding untreated, gas or fluoric acid treatments. The wettability as well as the decay rate for the formic acid treated electrodes are less pronounced than most of the electrodes obtained for durability tests.

Further studies on the role of gases and high temperature on some selected samples, which have shown enhanced activities and stability are to be carried out in order to characterise and determine reactivity, porosity, textural and chemical properties both before and after electrochemical tests of the carbons.

Acknowledgements

References

[1] Y. Suzuki, M. Maeda, T. Yamada, T. Kimura, A. Hagiwara, H. Sotouchi, H. Sato, Electrochemistry 68 (2000) 181.

[2] H. Abe, T. Murai, K. Zaghib, J. Power Sources 77 (1999) 110.

[3] K.S. Yoo, B. Miller, R. Kalish, X. Shi, Electrochem. Solid State Lett. 5 (1999) 233.

[4] L. Duclaux, E. Frackowiak, F. Béguin, J. Power Sources 81/82 (1999) 323.

[5] M. Noel, R. Santhanam, J. Power Sources 72 (1998) 53.

[6] D. Qu, H. Shi, J. Power Sources 74 (1998) 99.

[7] K. Kordesch, K. Tomantschger, J. Power Sources 25 (1989) 195.

[8] J.B. Goodenough, A.K. Shukla, C.A.D.S. Paliteiro, K.R. Jamieson, A. Hamnett, R. Manoharan, Patent GB 2164 785A.

[9] M. Watanabe, K. Makita, H. Usami, S. Motoo, J. Electroanal. Chem. 197 (1986) 195.

[10] J. Mrha, Coll. Czech. Chem. Commun. 32 (1967) 708.

[11] K. Kordesch, S. Jahangir, M. Schautz, Electrochim. Acta 29 (1984) 1589.

[12] K. Kinoshita, in: S. Sarangapani, J.R. Akridge, B. Schumm, (Eds.), Proceedings of the Workshop of The Electrochemistry of Carbon, The Electrochemical Society, Pennington, NJ, USA,1984, p. 273.

[13] D.B. Fischbach, in: P.L. Walker, (Ed.), Chemistry and Physics of Carbon, Vol. 7, Dekker, New York, 1971, p. 107.

[14] J.J. Freeman, F.G.R. Gimblett, R.A. Roberts, K.S.W. Sing, Carbon 25 (1987) 559.

[15] P.N. Ross, M. Sattler, J. Electrochem. Soc. 135 (1988) 1464.

[16] A.J. Appleby, J. Marie, Electrochim. Acta 24 (1979) 195.

[17] J.M. Solar, C.A. Leon y Leon, K. Osseso-Asare, L.R. Radovic, Carbon 28 (1990) 369.

[18] J. McBreen, H. Olender, S. Srinivasan, K.V. Kordesch, J. Appl. Electrochem. 11 (1981) 787.

[19] Y. Kiros, S. Schwartz, J. Power Sources 36 (1991) 547.

[20] H. Marsh, Introduction to Carbon Science, Butterworths, London, 1989, p. 112.

[21] J.B. Byrne, H. Marsh, in: J.W. Patrick (Ed.), Porosity in Carbons, Edward Arnold, London, 1995, p. 16.

[22] T. Murata, Y. Matsuda, Electrochim. Acta 27 (1982) 795.

[23] J.S. Noh, J.A. Schwartz, J. Colloid Interf. Sci. 130 (1989) 137.

[24] T.J. Fabish, D.E. Schleifer, Carbon 22 (1984) 19.

[25] K. Kinoshita, Carbon electrochemical and Physicochemical Properties, Wiley, New York, 1988, p. 101.

[26] K. Kinoshita, Carbon electrochemical and Physicochemical Properties, Wiley, New York, 1988, p. 97.

[27] A. Frennet, P.B. Wells, Appl. Catal. 18 (1985) 243.

[28] J.A. Konvalinda, P.H. Van Oeffelt, J.J.F. Scholten, Appl. Catal. 1 (1981) 141.

[29] Technical Bulletin, Ketjenblack EC Akzocehmie, 1996, p. 8.

[30] M. Maja, C. Orecchia, M. Strano, P. Tosco, M. Vanni, Electrochim. Acta 46 (2000) 423.

[31] E. Yeager, J.A. Molla, S. Gupta, in: S. Sarangapani, J.R. Akridge, B. Schumm, (Eds.), Proceedings of the Workshop on the Electrochemistry of Carbon, The Electrochemical Society, Pennington, NJ, 1984, p. 123.