

Serial No. 621,404
Filing Date 25 March 1996
Inventor Debra R. Rolison
Karen E. Swider

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LOW TEMPERATURE CATALYTIC DESULFURIZATION OF CARBON-BASED
MATERIALS, AND THE USE OF LOW SULFUR-CONTENT CARBON IN POWER
SOURCE APPLICATIONS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to improvements in the lifetimes of carbon-supported electrodes used in fuel cells and batteries by the removal of low-valent sulfur (which acts as a catalytic poison) from the carbon in these electrodes, through a catalytic process. The invention also relates to removing sulfur from coal and other carbon blacks. The invention also relates to producing sulfate ion.

Description of the Related Art

As used herein, "low-valent sulfur" refers to sulfur in a zero or negative oxidation state. This includes, but is not limited to, zero-valent organic sulfur (sulfur covalently bonded to carbon, but not to oxygen). Such organic sulfur may be part of an organic ring or chain (typically 5- or 6- membered heterocyclic rings). Most typically, organic sulfur will be part of an aromatic group like thiophene or thiophene derivatives. Low-valent sulfur also includes negative valence species such as metal sulfides (e.g., CoS, FeS, FeS₂), and hydrogen sulfide H₂S. These species may be

1 found in carbon samples as impurities, where they may be dissolved, agglomerated, adsorbed, etc.

2 As used herein, the term "sulfur-containing carbon" refers to all of these species.

3
4 Referring to FIG. 8, fuel cells 50 are devices that produce electricity from electrochemical
5 reactions. The reactants in fuel cells are replenished as needed, typically in a continuous flow
6 process. Consequently, fuel cells 50 generally have one or more inlet ports 52 for reactants (i.e.,
7 the fuel and the oxidant), and an outlet port 54 for the reaction products, in the reaction vessel
8 56. All fuel cells have, in the reaction vessel, an anode 58 and a cathode 60, which are separated
9 from each other by an electrolyte 59. In the fuel cell art, the term "electrolyte" is used in its
10 broadest sense: a material, composition, or structure that passes ions but not electrons between
11 the two electrodes. Most modern fuel cell electrolytes are solid phase, such as polymer mem-
12 branes, although liquid electrolytes for fuel cells are also known. Some exemplary solid phase
13 electrolytes include sulfonated fluorocarbon polymers such as Nafion™ (DuPont), and ceramic
14 oxides such as yttria-stabilized zirconia ($Y_2O_3 \cdot ZrO_2$, a.k.a. YSZ)

15 The electrodes used for fuel cells typically use some type of noble metal or noble metal
16 alloy as a catalyst. These are referred to in the art as electrocatalysts. Common electrocatalysts
17 include platinum metal (e.g., platinum black), platinum alloys (such as PtSn, PtRu, and multiple
18 ternary platinum alloys), and cobalt-centered macrocycles. For a variety of reasons, in particular
19 the high cost of many of these electrocatalysts, it is typical to put the electrocatalyst on a carbon
20 matrix. This can be done by mixing the electrocatalyst with a carbon matrix, or supporting the
21 electrocatalyst on a carbon support matrix. A particularly common electrode, ca. 25 Å Pt metal

1 clusters on a vulcan carbon support matrix is described in greater detail below. Some types of
2 carbon that have been used as matrices for electrocatalysts include vulcan carbon, pyrolytic
3 carbon, glassy carbon, and carbon blacks. Vulcan carbon is a form of carbon that contains low-
4 valent sulfur, due to its production process. It has a number of desirable properties, but, as
5 described below, it also has some undesirable properties for use as an electrocatalyst matrix.

6 Proton-exchange membrane fuel cells (PEMFCs) are an attractive alternative to petroleum-
7 based energy sources. In these electrochemical cells, hydrogen is oxidized to protons at the
8 anode; the protons then transfer through the PEM and combine with reduced oxygen at the
9 cathode to form water. See generally A.J. Appleby and F.R. Foulkes, Fuel Cell Handbook, (Van
10 Nostrand Reinhold, New York) (1989) and H.P. Dhar, J. Electroanal. Chem., **357**, 237 (1993),
11 both of which are incorporated by reference herein. These oxidation and reduction reactions are
12 catalyzed at the fuel-cell electrodes by platinum or noble-metal alloys. To reduce the cost of the
13 electrodes, the traditional Pt-black electrodes of PEMFCs and phosphoric acid fuel cells (PAFCs)
14 have been replaced by carbon-supported noble-metal clusters. By using clusters on the order of
15 25 Å in diameter instead of noble metal blacks, the mass activity of the noble metal is dramatical-
16 ly increased. See K. Kinoshita, J. Electrochem. Soc., **137**, 845 (1990).

17 A chronic concern in the engineering of a fuel cell is to prevent poisoning of the electrode
18 catalysts, particularly by sulfur. One source of sulfur is H₂S gas, a common impurity in fuel gas.
19 The sulfurous gas dissociatively adsorbs on the Pt surface and then blocks the available sites for
20 catalysis of the fuel. See D-T. Chin and P.D. Howard, J. Electrochem. Soc., **133**, 2447 (1986),

1 and J. Biswas et al. Catal. Rev. - Sci. Eng. 30, 161 (1988), both of which are incorporated by
2 reference herein.

3 Another source of sulfur in fuel cell electrodes comes from the carbon support. In the
4 vulcanized carbon that is favored as a support--due to vulcan carbon's high electronic conductivi-
5 ty (especially relative to other carbon blacks) and surface properties (e.g., wetting behavior) (see
6 J. McBreen et al., J. Appl. Electrochem., 11, 787 (1981), incorporated by reference herein)--there
7 is approximately 5000 ppm (weight) of sulfur. See K. Kinoshita, Carbon: Electrochemical and
8 Physicochemical Properties (John Wiley and Sons, New York) (1988), G. Tamizhmani and G.A.
9 Capuano, J. Electrochem. Soc., 141, L132 (1994), both of which are incorporated by reference
10 herein. This corresponds to one sulfur atom for every 3.3 platinum atoms in a typical 10 wt%
11 Pt/carbon electrocatalyst (see Kinoshita et al., J. Electrochem. Soc. 137 845 (1990), incorporated
12 by reference herein), so the ratio of Pt surface atoms to S atoms is *ca.* 1.5 to 1 in a 10 wt%
13 Pt/carbon material. Because a single sulfur atom can poison multiple Pt sites (see J. Biswas et
14 al., *supra*, and T.D. Halachev and E. Ruckenstein, Surf. Sci., 108, 292 (1981), both of which are
15 incorporated by reference herein), there is sufficient S in the vulcan carbon to poison the entire
16 surface area of the supported Pt clusters. Yet, the excellent initial performance of PAFCs and
17 PEMFCs and the low overpotentials observed at their anodes suggest that the sulfur in the carbon
18 support has no influence on the fuel cells, and this high concentration of native sulfur is generally
19 overlooked. Until now, it had not been shown that carbon-associated sulfur in fuel cell electrodes
20 would affect the performance of fuel cell electrocatalysts. Currently available Pt-C electrodes
21 lose 10-100% of their performance efficiency after about 6 months of use.

1 Referring to FIG. 9, batteries are conceptually and structurally similar to fuel cells, except
2 that they are closed systems--fuel normally is neither added to nor removed from batteries during
3 discharge or optional recharge (for rechargeable batteries). Thus, a battery 62 has an anode 64
4 and a cathode 66 separated by an electrolyte 65. Similar concerns for electrode lifetime apply
5 to batteries as apply to fuel cells. One immediate problem is that many batteries lose ca. 10%
6 of their total battery capacity after the first charge-discharge cycle, whereupon reasonably stable
7 performance results. Slightly different terminologies are used for batteries, however. Instead of
8 "electrocatalyst", practitioners in the battery art refer to "active material". Also, the roles of the
9 anode and the cathode are reversed during recharge.

10
11 A chronic barrier to the use of naturally occurring hydrocarbons (i.e., coal and crude
12 petroleum) as an energy source is the presence of environmentally unfriendly sulfur in these
13 substances. Techniques are available for removing sulfur from naturally occurring hydrocarbons,
14 including thiophene-like sulfur or S that is covalently bonded to carbon atoms. However, many
15 of these procedures require elevated temperatures ($>100^{\circ}\text{C}$), or long times to achieve desulfur-
16 ization. One proposed method (see S.B. Lalvani et al., *Fuel Processing Tech.* **21** 117-123 (1989))
17 performs this process electrochemically, but teaches that a highly concentrated electrolyte solution
18 (1 M NaOH) is required. It is generally undesirable to carry out industrial processes in
19 electrolytes of high ionic strength (e.g., concentration ≥ 1 M of acid, base, or salt solutions), for
20 reasons including cost, workplace safety, and pollution control.

1 Sulfuric acid, an important commercial reagent, is commonly manufactured by hydrogenation of sulfate (SO_4^{2-}) ion. Accordingly, commercial processes for the production of sulfate are
2 desired.
3

4
5 SUMMARY OF THE INVENTION

6 Accordingly, it is an object of this invention to remove S, especially low-valent S, from
7 carbon contaminated with low-valent S.

8 It is a further object of this invention to extend the useful lifetimes of electrodes used in
9 batteries and fuel cells, by preventing the catalytic poisoning effect arising from S contained in
10 the carbon matrices of these electrodes.

11 It is a further object of this invention to provide a low-cost method for producing oxidized
12 S, in particular sulfate (SO_4^{2-}) ion, which is an industrial precursor for H_2SO_4 .

13 It is a further object of this invention to achieve each of these goals at ambient or near
14 ambient temperatures, under mild chemical conditions and low ionic concentrations (e.g., ca.
15 0.05 M electrolyte)

16 These and additional objects of the invention are accomplished by the structures and
17 processes hereinafter described.

18 The present invention is, in one aspect, a process for removing low-valent sulfur from
19 carbon containing such low-valent sulfur (sulfur-containing carbon), having the step of contacting
20 the sulfur-containing carbon with a platinum oxide in an aqueous environment, for a time

1 sufficient to remove a desired amount of low-valent sulfur from the sulfur-containing carbon,
2 especially from the surface of the carbon.

3 Another aspect of the invention is an electrode, comprising an electrocatalyst or active
4 material for a fuel cell or battery, disposed in a carbon matrix, where the carbon matrix is
5 essentially free of low-valent sulfur adjacent to the active material of the battery electrode or
6 electrocatalyst of the fuel cell electrode. Such an electrode will be suitable for use in a fuel cell
7 or in a battery.

8 Another aspect of the invention is a fuel cell, comprising: (a) a fuel cell reaction vessel
9 having an output port for removing reaction products, and at least one input port for introducing
10 reactants, where the fuel cell reaction vessel contains an electrolyte, (b) a cathode disposed within
11 the reaction vessel and (c) an anode disposed within the reaction vessel, where at least one of the
12 electrodes comprises an electrocatalyst (typically a noble metal or noble metal alloy) in contact
13 with a carbon matrix, where this carbon matrix is essentially free of low-valent sulfur adjacent
14 to the electrocatalyst, and where the electrodes are separated by the electrolyte.

15 Another aspect of the invention is a method of generating electricity from a fuel cell,
16 comprising: (a) introducing a fuel and an oxidant into a fuel cell reaction vessel containing an
17 electrolyte, (b) reducing the oxidant at a cathode in the reaction vessel, (c) oxidizing the fuel at
18 an anode in the reaction vessel, where at least one of the electrodes comprises an electrocatalyst
19 (typically a noble metal or noble-metal alloy) in contact with a carbon matrix, where this carbon
20 matrix is essentially free of low-valent sulfur adjacent to the electrocatalyst, and where the

1 electrodes are separated by the electrolyte, and (d) removing products of the oxidation and the
2 reduction from the fuel cell.

3 Another aspect of the invention is a battery, comprising: (a) a vessel containing an electro-
4 lyte, (b) a cathode disposed within the vessel and (c) an anode disposed within the vessel, where
5 at least one of the electrodes comprises an active material (typically a metal chalcogenide, e.g.,
6 MO_x , MS_x , or MSe_x) in contact with a carbon matrix or a carbon-only matrix, where this carbon
7 matrix is essentially free of low-valent sulfur adjacent to the active material, and where the
8 electrodes are separated by the electrolyte.

9 Another aspect of the invention is a method for generating electricity from a battery,
10 comprising: (a) providing a reducing agent and an oxidant in a battery vessel containing an
11 electrolyte, (b) reducing the oxidant at a cathode in the battery vessel, and (c) oxidizing the
12 reducing agent at an anode in the battery vessel, where at least one of the electrodes comprises
13 an active material (typically a metal chalcogenide) in contact with a carbon matrix, where this
14 carbon matrix is essentially free of low-valent sulfur adjacent to the active material, and where
15 the electrodes are separated by the electrolyte.

16 Another aspect of the invention is a method for producing sulfate ion, comprising the
17 steps: (a) contacting carbon containing low-valent sulfur with a platinum oxide in an aqueous
18 environment, to convert the low-valent sulfur to sulfate ion; and (b) extracting the sulfate ion.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention will be obtained readily by reference to the following Description of the Preferred Embodiments and the accompanying drawings in which like numerals in different figures represent the same structures or elements, wherein:

FIG. 1 is a representation of a typical particle of sulfur-containing carbon.

FIG. 2 shows a cyclic voltammetry curve for platinum in H_2SO_4 .

FIG. 3 is a representation of an apparatus used to desulfonate carbon samples.

FIG. 4 is a flow chart showing the steps in a "mock" fuel-cell electrode preparation.

FIG. 5 is a series of XPS traces showing the S2p region of Pt/C.

FIG. 6 is a series of cyclic voltammetry traces.

FIG. 7 is a series of XPS traces showing excess sulfate in Pt/C.

FIG. 8 shows a cross-section of a fuel cell

FIG. 9 shows a cross-section of a battery.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

K.E. Swider et al., "The Chemical State of Sulfur in Carbon-Supported Fuel Cell Electrodes", J. Electrochem. Soc. **143** (3) (March 1996, in press), is incorporated by reference herein, in its entirety, for all purposes.

As noted above, vulcan carbon is a favored support for fuel cell electrocatalysts and battery active materials. It has been discovered that the vulcan carbon used to support platinum catalysts in electrodes contains high concentrations of the catalytic poison S, which is covalently

1 bonded to the carbon, as in carbon chains or rings. It has further been discovered that this
2 covalently bonded, zero-valence sulfur may be removed from this carbon (i.e., the covalent C-S
3 bonds may be broken) if the sulfur is brought into contact with oxidized Pt in the presence of
4 water and heat. It has further been discovered that this desulfurization may be done electro-
5 chemically, by maintaining a platinum electrode at a potential (volts vs. a reference potential) in
6 the oxide region of its current-voltage curve, preferably in low-ionic strength solution.

7 Thus, as shown in FIG. 1, a particle of sulfur-containing carbon 10 may typically have
8 sulfur atoms 12 that are in positions that are inaccessible to surrounding platinum particles (e.g.,
9 the sulfur atom may be in the interior of the particle 10). The particle of carbon 10 will also
10 typically have sulfur atoms 14 that are in positions that are accessible to surrounding platinum
11 particles (e.g., the sulfur atom may be at or near the exterior surface 13 of the particle 10). In
12 both of these cases, the sulfur atoms typically are covalently bonded to carbon atoms 16. It
13 should be noted, however, that the position of a given sulfur atom may change over time, and
14 with its position change, its accessibility by platinum may also change. When a Pt particle 18
15 contacts a sulfur atom 14 in the presence of water and heat, the S-C bonds are broken and the
16 sulfur is reduced to water soluble sulfate ion 20.

17 Referring to FIG. 2, this shows a cyclic voltammetry curve for platinum in H_2SO_4 . The
18 dashed lines have been added for illustration. The area between the two dashed lines is referred
19 to as the double layer region 22 of the cyclic voltammetry curve. To the left of this area is the
20 hydrogen region 24 of the cyclic voltammetry curve. To the right of this double layer area 22
21 is the oxide region 26 of the cyclic voltammetry curve. At the rightmost end of this oxide region,

1 the curve tips upward. This upwardly tipped region is the oxygen evolution portion 28 of the
2 cyclic voltammetry curve.

3 In a preferred method for removal of sulfur from carbon which contains sulfur, platinum
4 oxide is provided by putting a platinum electrode in a dilute acid, base, or ionic solution in the
5 oxide region of the current-voltage curve. In this part of the curve, as the name suggests,
6 platinum on the surface of this electrode will be in the form of a platinum oxide--PtO_x where
7 $0 < x < 2$, preferably where $ca. 0.5 \leq x \leq ca 1.0$. Typically, some type of ionic solution will be
8 used to assist in the formation of platinum oxide, as skilled practitioners will recognize. The
9 platinum oxide is put into contact with the carbon. During this contacting, low-valent sulfur
10 atoms that come into contact with platinum oxide will be oxidized to sulfate, which is soluble in
11 water. This sulfate can then be washed out.

12 Skilled practitioners will recognize that the location of the oxide region of the platinum
13 electrode will depend on the local environment of the platinum. For example, in mild acidic
14 conditions (e.g., ca. 0.05 M HNO₃) it is known that maintaining an electrode potential of about
15 1 volt versus a hydrogen reference is sufficient to keep Pt oxidized.

16 It has been discovered that, contrary to the teaching of Lalvani et al., it is not necessary
17 to use high potentials to remove sulfur from coal or other forms of carbon. See Lalvani et al.,
18 Fuel Processing Tech. 18 25-36 (1988). Lalvani uses a very high potential, in the oxygen
19 evolution portion of the cyclic voltammetry curve. It has been found that this is not only not
20 necessary, but somewhat counterproductive. It has also been found that contrary to the teaching
21 of Lalvani et al., it is not necessary to use high ionic strengths. Lalvani uses 1 M NaOH. In

1 contrast, half-molar, tenth-molar, and even hundredth-molar ion contents are sufficient, as long
2 as Pt is in the oxide region (preferably below the oxygen evolution region) of the current-voltage
3 curve.

4
5 A preferred electrode for use in power sources according to the invention has an electro-
6 catalyst or active material (as noted above, these two terms are used in the fuel cell art and
7 battery art, respectively), mixed with or supported on a carbon matrix, where the carbon
8 comprises carbon particles having a reduced concentration of sulfur atoms that are accessible to
9 platinum, compared to the 5000 ppm concentration of standard vulcan carbon. More preferably,
10 the concentration of sulfur atoms that are accessible to platinum is less than about 500 ppm. Still
11 more preferably, the concentration of sulfur atoms that are accessible to platinum is less than
12 about 50 ppm. Most preferably, the concentration of sulfur atoms that are accessible to platinum
13 is essentially zero.

14
15 A preferred fuel cell according to the invention uses the preferred electrode of the
16 invention as the anode and/or the cathode. In operation, the reduced sulfur content at the surface
17 of the carbon matrix retards the poisoning of the electrocatalyst. In the most preferred embodi-
18 ment of the invention, where the concentration of sulfur atoms at or near the surface of the
19 carbon particles is essentially zero, the electrocatalyst will avoid being poisoned until such time
20 as any remaining carbon-associated sulfur atoms that were initially inaccessible to the electro-
21 catalyst may migrate to positions or otherwise become accessible to the electrocatalyst, and subse-

1 quently poison the electrocatalyst. For example, if the carbon matrix partially decomposes,
2 previously inaccessible sulfur may become accessible. To date, fuel cell operation in excess of
3 1000 hours has been demonstrated consistently.

4
5 A preferred battery according to the present invention uses the preferred electrode of the
6 invention as the anode and/or the cathode. In operation, the reduced sulfur content at the surface
7 of the carbon matrix retards the poisoning of the active material. In the most preferred embodi-
8 ment of the invention, where the concentration of active material-accessible sulfur atoms is
9 essentially zero, the active material will avoid being poisoned until such time as any sulfur atoms
10 which were inaccessible become accessible to the active material, and subsequently poison the
11 active material.

12
13 To understand the behavior of the sulfur in carbon-supported platinum electrocatalysts,
14 we have examined its chemical state at different stages in the preparation of fuel-cell electrodes.
15 This is achieved in three ways: (1) by measuring the oxidation state of the sulfur in the
16 electrocatalysts using x-ray photoelectron spectroscopy (XPS); (2) by qualitatively monitoring the
17 presence of sulfate ion in the aqueous filtrate created after slurrying the electrode materials in
18 water; and (3) by examining the electrochemistry of the electrocatalysts. These results yield
19 information about the interaction of platinum with the sulfur impurities native to the vulcan
20 carbon and lead to suggestions about how to reduce possible poisoning of fuel-cell electrodes
21 during long-term operation.

1 Having described the invention, the following examples are given to illustrate specific
2 applications of the invention, including the best mode now known to perform the invention.
3 These specific examples are not intended to limit the scope of the invention described in this
4 application.

5
6 General Experimental Procedures and Standards

7 Four different materials have been analyzed. Vulcan carbon [XC-72] (Cabot) and
8 platinum black (fuel-cell grade Johnson Matthey) are used as baseline materials. A "model"
9 electrocatalyst is prepared by grinding together 10 wt% Pt black (having *ca.* 100-Å particles) with
10 the vulcan carbon, C_(XC-72). As an example of a typical fuel-cell electrocatalyst, we use 10% Pt
11 supported on C_(XC-72) (E-TEK). The Scherrer formula is used to analyze the peak broadening in
12 the x-ray diffraction patterns of the E-TEK electrocatalyst and to confirm the quoted Pt cluster
13 size of 25 Å.

14 A protocol has been developed involving water dispersion, hot pressing, and oven
15 annealing of the electrocatalysts to imitate the preparation of a typical fuel-cell electrode. See
16 H.P. Dhar, *supra*. The usual additions of flocculants, binders, and ionomers are omitted because
17 they interfere with the XPS measurements of carbon-associated sulfur, as discussed below.

18 The treatment steps in our "mock" fuel-cell electrode preparation is summarized in a flow
19 chart in FIG. 4. The symbol X⇒ indicates points at which samples were taken for the XPS,
20 Ba(OAc)₂, and cyclic voltammetry analyses. Approximately 0.5 g of the electrocatalyst materials
21 were dispersed in 100 mL of 18 MΩ-cm H₂O (Barnstead NanoPure) and ultrasonicated for a total

1 of 6 minutes (Sonics and Materials, Vibra Cell). The majority of the water was removed by
2 filtration, and then the material was hot pressed on filter paper at 100°C for 5 min at 1000 psi.
3 The electrocatalysts were then scraped from the filter paper into an Al boat and oven heated in
4 air stepwise at 100°C (1 hr), 200°C (1 hr), and 275°C (15 min). To examine the influence of the
5 heating procedures on the chemical state and content of the sulfur in the electrocatalysts, the
6 water dispersion and heating steps were repeated. In these cases, the electrocatalysts were ultra-
7 sonicated in water, hot pressed, and heated in air at 100°C (1 hr) and then once again dispersed
8 in H₂O, hot pressed, and heated in air at 100°C (1 hr), 200°C (1 hr), and 275°C (15 min). The
9 electrocatalysts were not heated over 100°C in the first half of this treatment to minimize the
10 carbon oxidation and particle sintering that could occur by repetitive heating at the higher
11 temperatures. For comparison to these water/heat treatments, the dry electrocatalysts were also
12 heated in air at 100°C (1 hr), 200°C (1 hr), and 275°C (15 min). It should be noted that heating
13 to temperatures $\geq \approx 100^\circ\text{C}$ are in all likelihood unnecessary to the desulfurization, but were done
14 to fully imitate the standard fuel cell electrode heat treatment steps.

15 At different stages of our mock fuel-cell electrode preparation (FIG. 4), the carbon-based
16 materials were pressed into 99.99% indium foil (Johnson Matthey) and examined using XPS
17 (Surface Science Instrument Model SSX-100-03 X-ray Photoelectron Spectrometer, Al K- α
18 x-rays). The energies of the photoelectron lines were referenced to the C1s line of the vulcan
19 carbon which is defined as graphite (C1s = 284.2 eV). See J.F. Moulder, W.F. Stickle, P.E.
20 Sobol, and K.D. Boben, Handbook of X-ray Photoelectron Spectroscopy, ed. J. Chastain, Perkin
21 Elmer Corp., Eden Prairie, MN (1992). Due to both the low concentration of sulfur in the vulcan

1 carbon (<1 atom%) and the weak photoelectron cross-section of sulfur ($\sigma_{\text{Scofield S2p}} = 1.677$ relative
2 to $\sigma_{\text{CLS}} = 1.000$) (see J.H. Scofield, J. Electron. Spectrosc. Relat. Phenom., 8, 129 (1976)), at least
3 40 scans are required to obtain a signal having $S/N > 1.5$ for the S2p photoelectron line (see
4 FIG. 5, discussed in greater detail below). In several cases, we assign "trace" peaks indicating
5 the possible presence of a low concentration of a sulfur species (<0.1 atom%). However, the
6 actual presence of these trace peaks may be disputed as they are at the noise level of the
7 background. The relative areas of elemental lines were determined using a χ^2 -minimization
8 routine and corrected for cross-sectional and instrumental factors.

9 The presence of sulfate ions in the filtrate of the treated catalyst is examined qualitatively
10 by the addition of aqueous barium acetate, $\text{Ba}(\text{OAc})_2$, to form the water-insoluble white precipi-
11 tate, BaSO_4 . Filtrate is created from a water dispersion of the C(XC-72) and Pt/C(XC-72)
12 materials after different stages of their treatment as described above. The processed materials are
13 subjected to gravity filtration, and the resulting water is filtered again through a 0.45- μm
14 membrane filter (Acrodisk) to remove extraneous carbon. Several milligrams of $\text{Ba}(\text{OAc})_2$ are
15 then dissolved in the filtrate and the formation of BaSO_4 precipitates is visually monitored. A
16 clear solution results from a $\text{Ba}(\text{OAc})_2$ test of filtered 18 M Ω -cm H_2O . A visibly cloudy solution
17 indicates the presence of ≥ 8 ppm sulfate ion.

18 The variously treated Pt/C(XC-72) powders are prepared for electrochemical analysis by
19 pressing them into the pinholes of a slightly porous glassy-carbon electrode. The Pt/C(XC-72)-
20 modified glassy-carbon electrodes are submerged in de-aerated 0.1 M H_2SO_4 vs. a Pt-wire
21 auxiliary electrode and referenced to a Pd/H electrode. The cyclic voltammetric response is

1 measured using a potentiostat (EG&G PAR model 173) and waveform sweep programmer
2 (EG&G PAR model 175). A cycle is started at the open-circuit potential of the cell and is swept
3 negative at 0.05 V/s to -0.01 V vs. Pd/H to map the initial state of the hydrogen adsorption sites
4 on the platinum. The positive potential of the measurements is limited to 1.0 V to avoid
5 extensive oxidation of the carbon.

6 FIG. 5 shows the XPS analysis of the S2p region of 10% Pt-black/C_(XC-72) materials.
7 Curve *a* shows VC1 (as-received vulcan carbon); curve *b* shows PTBC1 (as-ground 10% Pt-
8 black/C_(XC-72)); *c*: PTBC3 (10% Pt-black/C_(XC-72) after water dispersion and hot pressing); *d*:
9 PTBC4 (10% Pt-black/C_(XC-72) after water dispersion, hot pressing, and oven heating); *e*: PTBC5
10 (10% Pt-black/C_(XC-72) after two treatments of water dispersion, hot pressing, and oven heating).
11 The sample treatments and XPS results are summarized in Table I. Photoelectron lines at 163.8
12 and 168.2 eV are assigned to zero-valent organosulfur and sulfate species, respectively. The
13 S2p_{3/2} and 2p_{1/2} components are resolvable for these photoelectron lines and are shown by the
14 dashed line. The calculated fit for the S2p envelope is indicated by -o-.

15 FIG. 6 shows a series of cyclic voltammetry traces for the experiments described below.

16 FIG. 7 shows a series of XPS traces showing the excess sulfate in Pt/C materials. Curve
17 *a* shows as-received 10% Pt/C_(XC-72) commercial catalyst [E-TEK] which has been synthesized
18 from sulfate-based Pt precursors. Curve *b* shows 10% Pt-black/C_(XC-72) which has been water
19 suspended using H₂SO₄ as a flocculant; Curve *c* shows VC4 (vulcan carbon after two treatments
20 of water dispersion, hot pressing, and oven heating).
21

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Example 2:
Establishing that the Platinum in Fuel-Cell Electrodes Interacts
with the Sulfur in the Vulcan Carbon.

Vulcan carbon was treated using the typical water and heat processing steps used to make a fuel-cell electrode, and XPS indicated that the chemical state and concentration of sulfur in the vulcan carbon was unchanged. See results in Table I: samples VC1 to VC4.

Platinum black was mixed with (or, in another experiment, Pt-clusters were supported on) vulcan carbon, and subjected to the same water and heat processing steps, and some of the sulfur in the vulcan carbon was oxidized to sulfate. This was verified using both XPS and a qualitative barium acetate, $\text{Ba}(\text{OAc})_2$, precipitation test for sulfate in the wash from the Pt/carbon mixtures. See results in Table I: samples PTCE3 and PTBC4.

Example 3:

Establishing that platinum oxidizes the carbon-associated sulfur
only under certain conditions

We have shown that sulfate is not generated when water is not added to the Pt/carbon mixtures during processing. See Table I: PTCE2, PTBC2.

We have also shown that sulfate does not form if the platinum and carbon do not come in contact during processing: (1) a slurry of water and platinum heated to 100 °C for 1 hour tested negative for sulfate; (2) additional water and heat processing of the Pt/carbon mixtures generated no new sulfate, presumably because the Pt has reacted with all of the sulfur in its immediate environment (see results in Table I: PTCE4, PTBC5 and FIG. 1).

We have also shown that a platinum oxide (PtO_x , $0 < x < 2$) is needed for the sulfur oxidation: (1) XPS and cyclic voltammetry indicate that a Pt-oxide species is always present in the electrochemically active Pt/C materials (FIG. 6, traces c, e, and f); (2) when carbon slurries come in contact with a Pt-mesh electrode, the oxidation of the carbon-associated sulfur occurs only when a Pt-oxide is electrochemically stabilized on the electrode surface. These experiments are highlighted below.

Example 4:

Establishing that the sulfate does not poison the fuel-cell electrochemistry

Commercial Pt/C electrocatalysts (E-TEK) exhibit excellent electrocatalytic behavior even though they are synthesized from sulfate-based precursors and contain large amounts of excess

1 sulfate, as we have shown. See Table I: PTCE1, and FIGS. 7 (trace a), and 6 (trace c). Further-
2 more, commercial Pt/C electrocatalyst having high concentrations of sulfate exhibits electrochem-
3 istry similar to that of Pt black (FIG. 6, trace a).

4 We have shown that when Pt/C mixtures are water and heat treated such that sulfate is
5 generated, their electrochemistry is identical to that of the starting materials. See FIG. 6, traces
6 c, e, and f.

7
8 Example 5:
9 Establishing that sulfur poisons the electrocatalysts.

10
11 It is known that sulfur poisons the noble metals. Previous research shows that H₂S gas
12 (a source of low-valent sulfur) poisons the electrocatalytic properties of Pt in PAFCs. C. The
13 sulfur in vulcan carbon can poison the Pt electrochemistry under certain conditions. EXAMPLE:
14 The platinum electrochemistry is compromised in Pt/C mixtures when they are heated in the
15 absence of water and the oxidation of the sulfur to sulfate does not occur. See Table I: PTCE2,
16 PTBC2 and FIG. 6, trace d. The Pt electrochemistry is *not* compromised in Pt/C mixtures when
17 they are heated in the absence of H₂O if the carbon has a low sulfur content (e.g., partially
18 desulfurized vulcan carbon or acetylene black). See FIG. 8, traces g and h.

19
20 Example 6:
21 Establishing that the sulfur in vulcan carbon may shorten the lifetime of fuel-cells.

22
23 We have shown that only the carbon-associated sulfur which comes in contact with the
24 Pt during the preparation of fuel cell electrodes, in the presence of water and heat, is oxidized

1 to sulfate, and the remaining sulfur remains in the electrode materials as zero-valent sulfur. See
2 Table I, PTCE3, PTCE4, PTBC4, and PTBC5.

3 Physicochemical conditions known to occur in operating platinum-catalyzed fuel cells will
4 create new contact of Pt with carbon-associated sulfur in environments in which the combination
5 of PtO_x , water, and temperature may not be optimal to oxidize the low-valent sulfur to innocuous
6 sulfate ions. For example: the Pt electrocatalyst clusters move on the vulcan carbon support
7 during the operation of a fuel cell and will therefore come in contact with new regions of
8 unreacted sulfur over time. Reducing conditions exist at the cathode, which may inhibit the
9 continued oxidation of the carbon-associated sulfur to sulfate by PtO_x and allow the sulfur to
10 poison the Pt surface. The anode can become "water-starved," a condition which could inhibit
11 the oxidation of the carbon-associated sulfur to sulfate by PtO_x and allow the sulfur to poison the
12 Pt surface.

13
14 General Experimental Procedures and Standards (Desulfonation Examples)

15 Referring to FIG. 3, the apparatus used to desulfonate carbon samples included a four-
16 aperture flask on a heater. The flask contained a 0.05 M solution of HNO_3 (about 50 ml), and
17 0.5 g vulcan carbon. The cathode and anode were high surface area electrodes, and were inserted
18 into the reaction flask through two of the ports. A hydrogen reference electrode (Pd/H) was
19 inserted in the third port, and the fourth port held a water-cooled condenser, to reflux any water
20 vapor back into the flask. The solution was then heated to about 100°C

Example 7:
Desulfurization of Carbon Samples

The procedures outlined above were followed at potentials of 0.5, 1.0, and 1.3 V vs. a Pd/H electrode. Results are shown in Table II.

Table I. Results from XPS and Ba(OAc)₂ analyses of various vulcan carbon and Pt-vulcan carbon powders after water and heat treatments.

sample name	sample description	B.E. (eV)		at%		presence of BaSO ₄
		S 2p	S ^{x+} 2p	S 2p	S	
PTB	Pt-black	n/a	n/a	--	--	n/a
PTBC1	10%Pt-black/C	163.60.3	168.80.3*	0.350.06	0.350.06	no
PTBC2	Δ	164.0	--	0.32	0.32	no
PTBC3	≈ ↓	163.60.1	168.30.2	0.440.06	0.360.04	no
PTBC4	≈ ↓ Δ	163.60.1	168.20.8	0.430.06	0.330.04	yes
PTBC5	≈ ↓ ○ ≈ ↓ Δ	163.60.3	168.10.3	0.440.08	0.390.07	no
PTCE1	10%Pt/C (E-TEK)	164.0	168.5	1.04	0.42	yes
PTCE2	Δ	163.9	168.2	0.76	0.46	no
PTCE3	≈ ↓ Δ	163.80.2	168.00.2	0.810.12	0.360.02	yes
PTCE4	≈ ↓ ○ ≈ ↓ Δ	163.70.1	168.50.4	0.980.23	0.370.08	no
VC1	C (XC-72)	163.9	--	0.36	0.36	no
VC2	≈ ↓	163.8	169.1*	0.42	0.34	no
VC3	≈ ↓ Δ	163.9	--	0.37	0.37	no
VC4	≈ ↓ ○ ≈ ↓ Δ	163.7	169.1*	0.44	0.36	no

The atomic percentages are calculated relative to the carbon peak. The sample treatments are summarized using the following notation:

≈ = dispersion in water

↓ = hot pressing

Δ = oven treatment in air at 100 C (1 hr), 200 C (1 hr), and 275 C (15 min)

○ = oven treatment in air at 100 C (1 hr).

The order of the symbols represents the sequence in which the procedures are executed.

* A trace amount (<0.1 atom %) of a high valence S-oxygen species (sulfate) may be present.

n/a = not applicable

Table II: Desulfurizations at various potentials

time↓	potential→	0.5 V vs. Pd/H	1.0 V vs. Pd/H	1.3 V vs. Pd/H
		(Pt ^o)	(PtO _x)	(PtO ₂ , O ₂ evolution)
1 hr		no SO ₄ ²⁻	SO ₄ ²⁻	no SO ₄ ²⁻
3 hr			additional SO ₄ ²⁻ , almost no S ^o	

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that

the invention may be practiced otherwise than as specifically described.

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Navy Case No. 77,413
Inventor(s): Rolison et al.

PATENT APPLICATION

ABSTRACT OF THE DISCLOSURE

The present invention is, in one aspect, a process for removing low-valent sulfur from carbon containing such low-valent sulfur (sulfur-containing carbon), having the step of contacting the sulfur-containing carbon with a platinum oxide in an aqueous environment, for a time sufficient to remove a desired amount of low-valent sulfur from the sulfur-containing carbon, especially from the surface of the carbon. Another aspect of the invention is an electrode, comprising an electrocatalyst or active material for a fuel cell or battery, disposed in a carbon matrix, where the carbon matrix is essentially free of low-valent sulfur adjacent to the active material of the battery electrode or electrocatalyst of the fuel cell electrode. Such an electrode will be suitable for use in a fuel cell or in a battery. Another aspect of the invention is a fuel cell or a battery using this electrode.

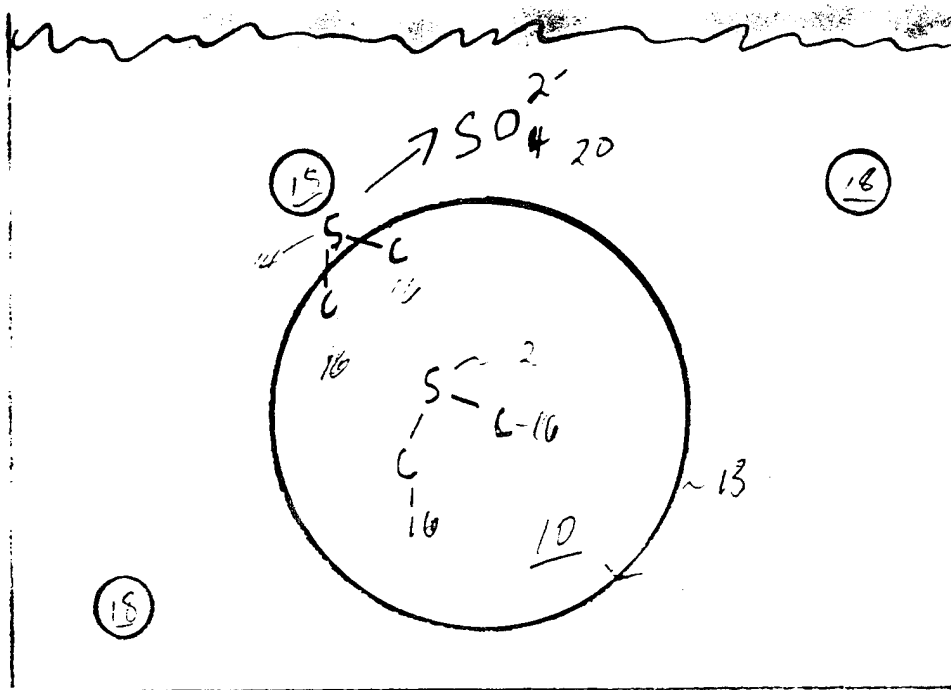
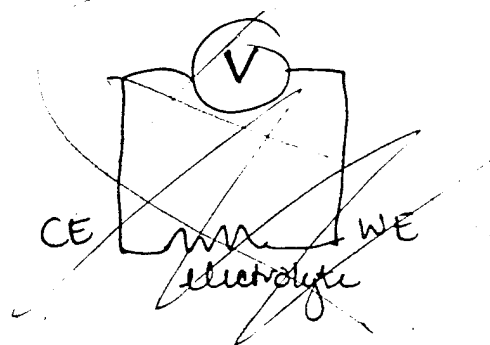
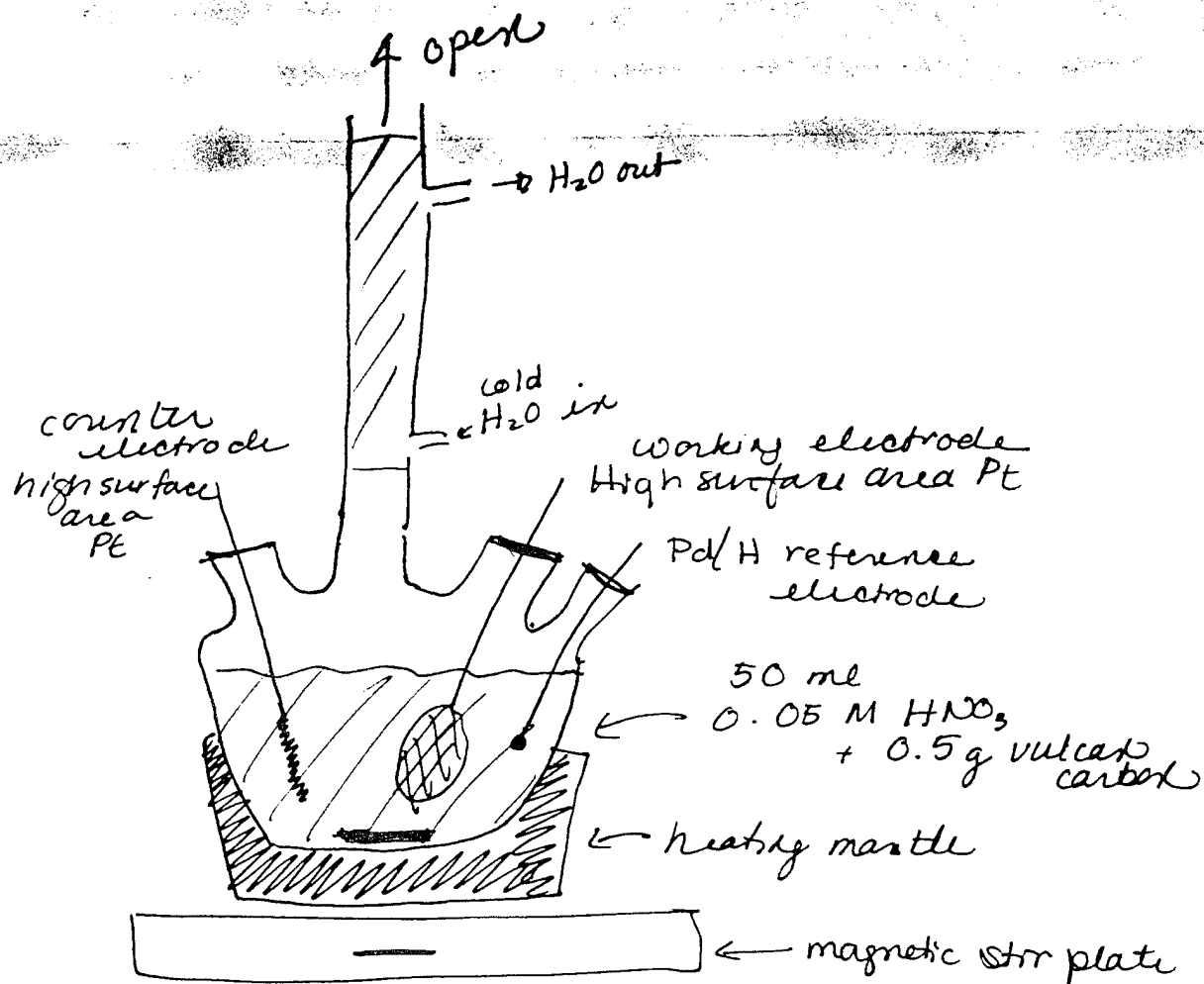


FIG. 1



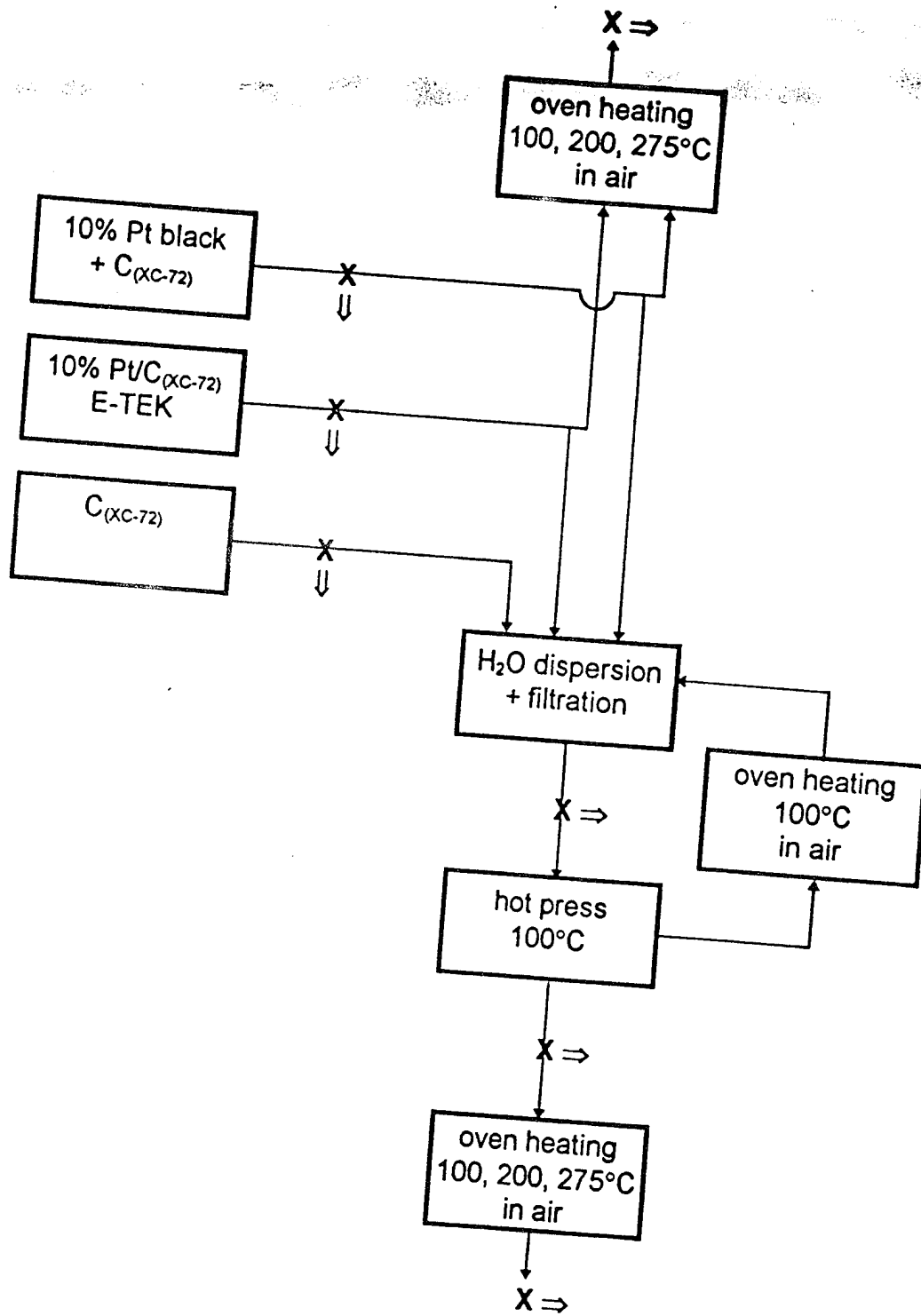


Fig 4

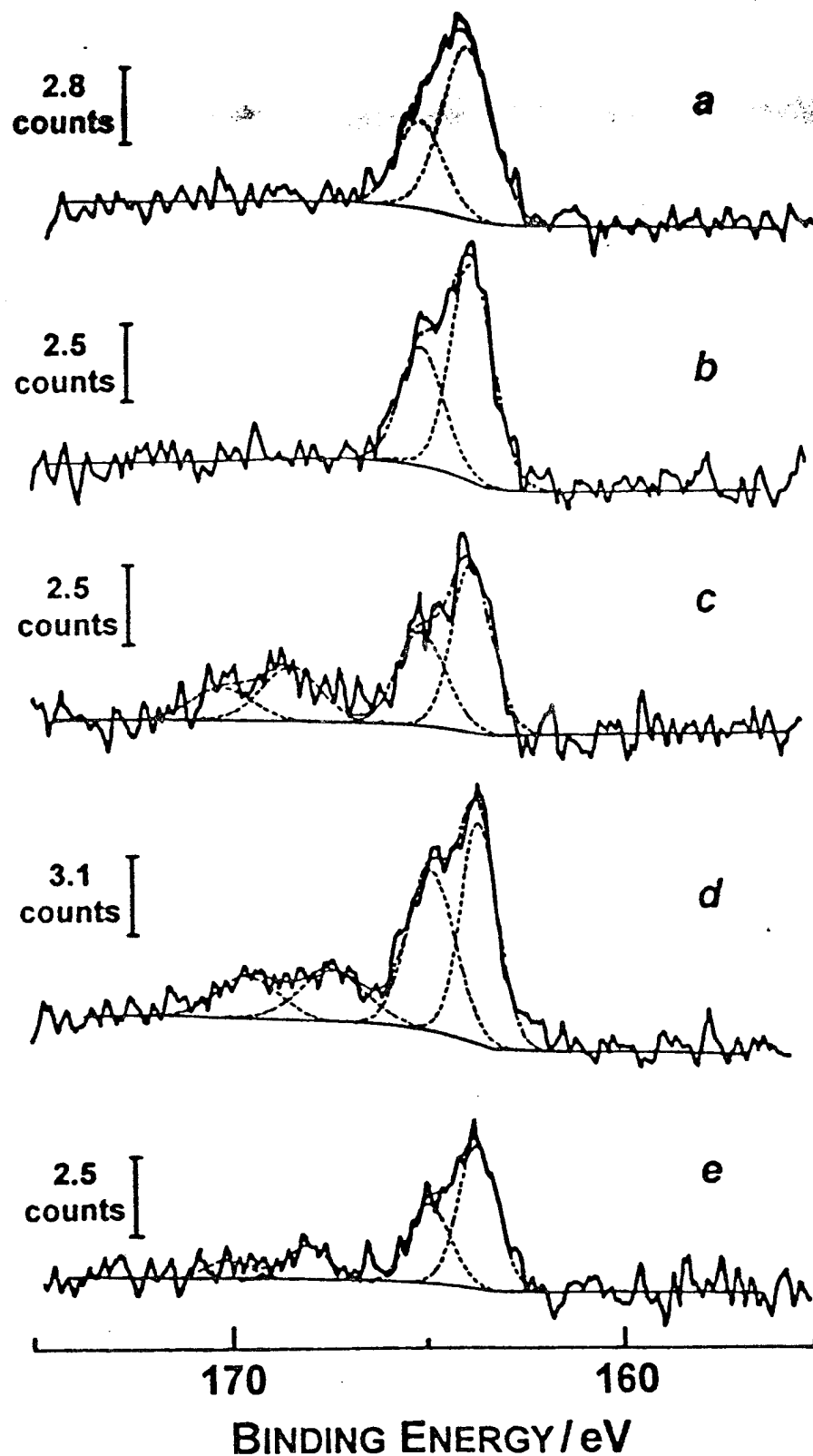


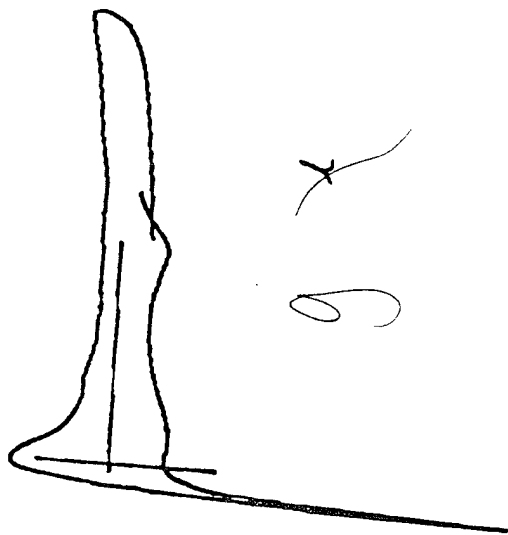
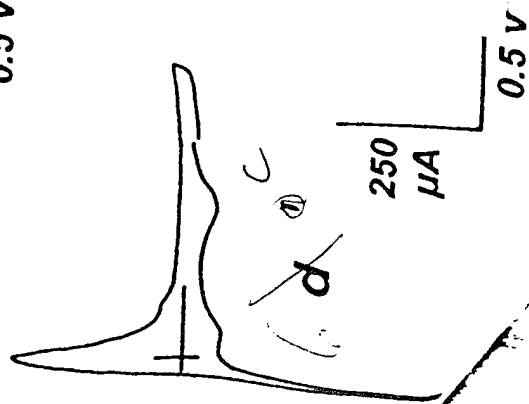
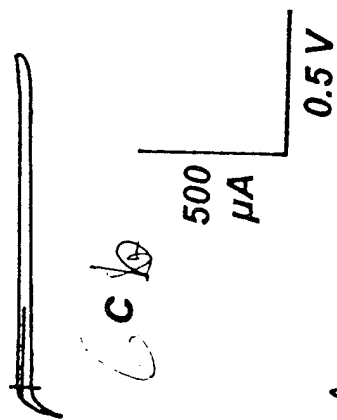
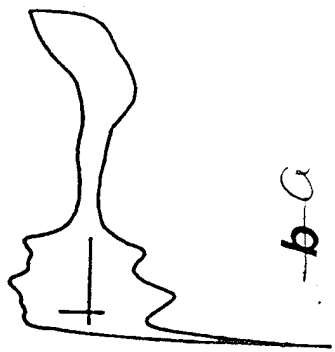
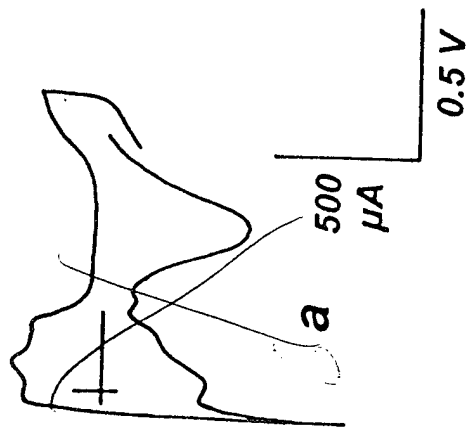
Fig. 5. XPS analysis of the S2p region of 10% Pt-black/ C_{XC-72} materials: a: VC1 (as-received vulcan carbon); b: PTBC1 (as-ground 10% Pt-black/ C_{XC-72}); c: PTBC3 [10% Pt-black/ C_{XC-72} after water dispersion and hot pressing]; d: PTBC4 [10% Pt-black/ C_{XC-72} after water dispersion, hot pressing, and oven heating]; e: PTBC5 [10% Pt-black/ C_{XC-72} after two treatments of water dispersion, hot pressing, and oven heating]. The sample treatments and XPS results are summarized in Table I. Photoelectron lines at 163.8 and 168.2 eV are assigned to S^0 and sulfate species, respectively. The $S2p_{3/2}$ and $2p_{1/2}$ components are resolvable for these photoelectron lines and are shown by the dashed line. The calculated fit for the S2p envelope is indicated by (—•—).

FIG. 5

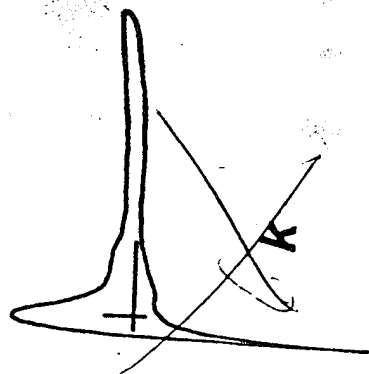
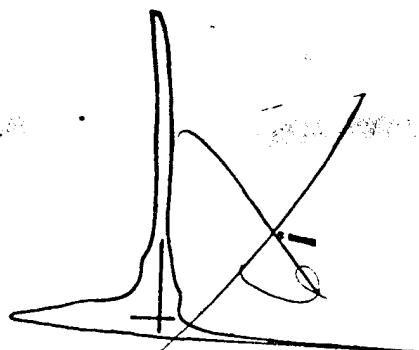
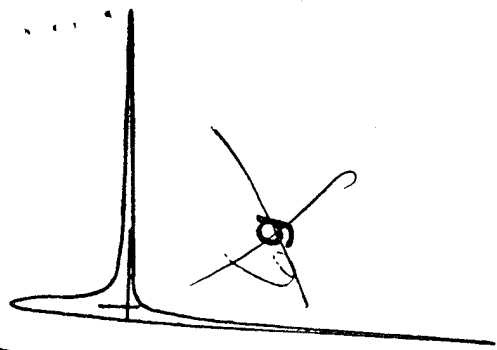
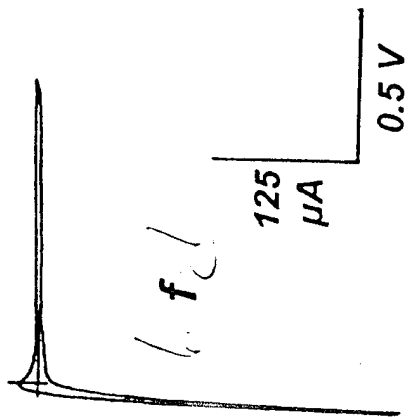
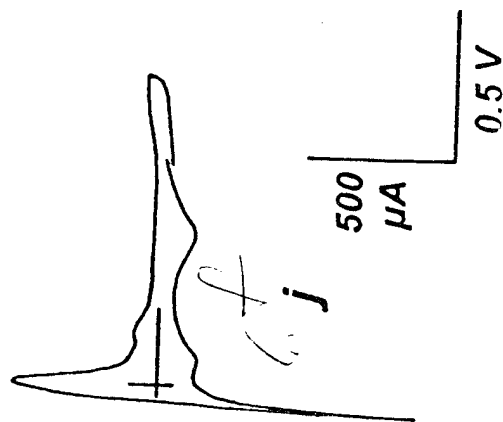
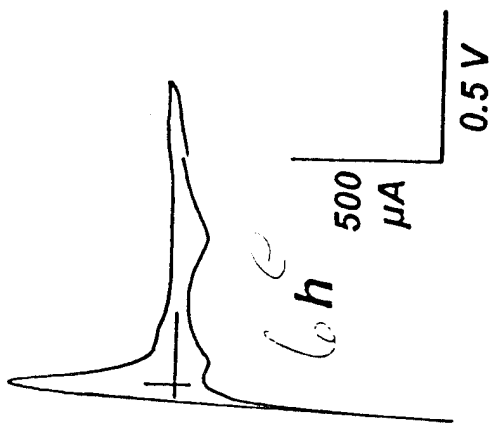
As a control, the vulcan carbon is subjected to the same water and heat treatments. Suspension of the C_{XC-72} in water and heating via hot pressing (VC2) produces a trace peak at 169.1 eV corresponding to a sulfate-like species. This sulfate peak is not observed if the water-filtered C_{XC-72} is hot pressed and oven heated (VC3), but it is present, again only at trace levels, if the water and heat-treatments are repeated (VC4, see Fig. 3c). Therefore, in the absence of Pt, a negligible amount of the zero-valent sulfur in vulcan carbon is oxidized to sulfate by water

and heat-treatments. This indicates that Pt is a catalyst for the oxidation of sulfur in vulcan carbon when exposed to water in the presence of heat. The active form of the catalyst may actually be the Pt(II) oxide present on the small clusters of supported Pt or the ca. 10 nm sized particles of Pt black, but we shall continue to refer to the system as Pt.

Additional observations suggest that this proposed platinum-catalyzed sulfur oxidation reaction relies upon close contact of the Pt with the vulcan carbon. In several of our



g



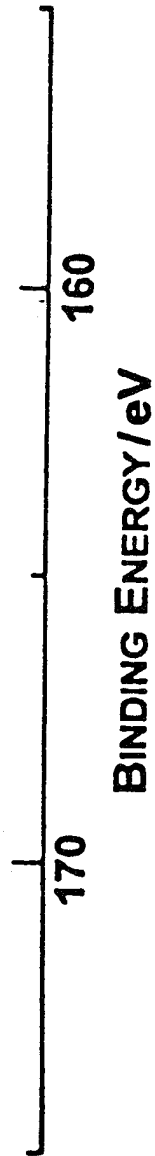
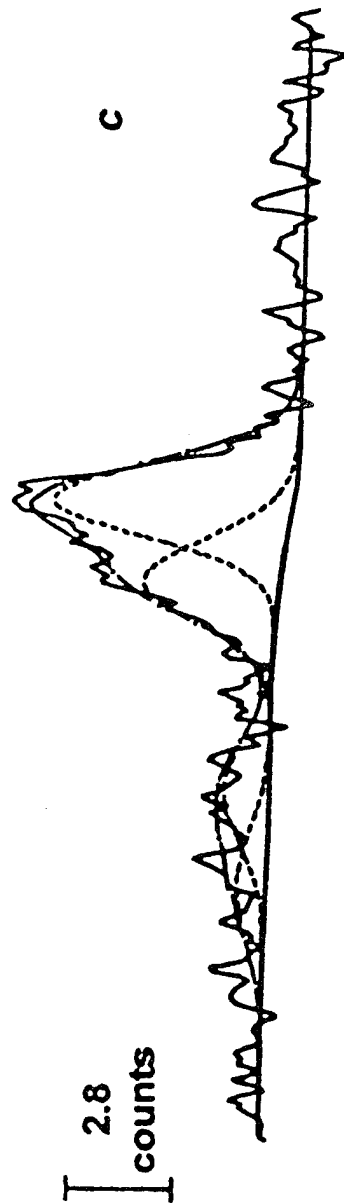
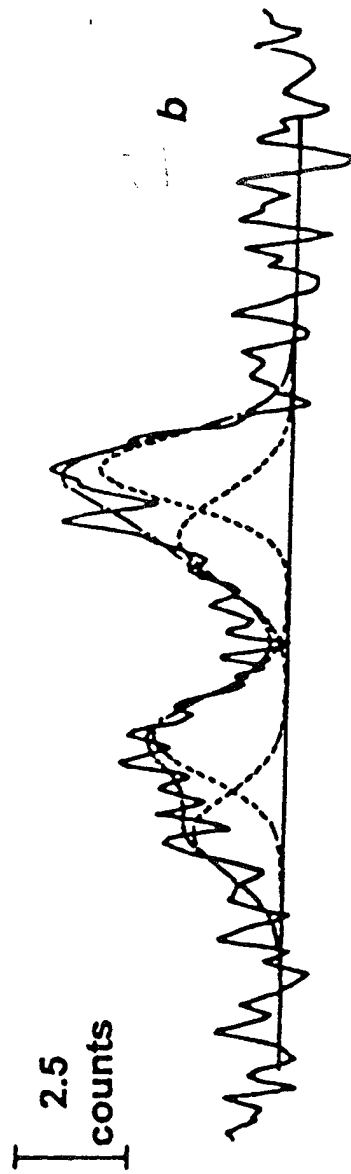
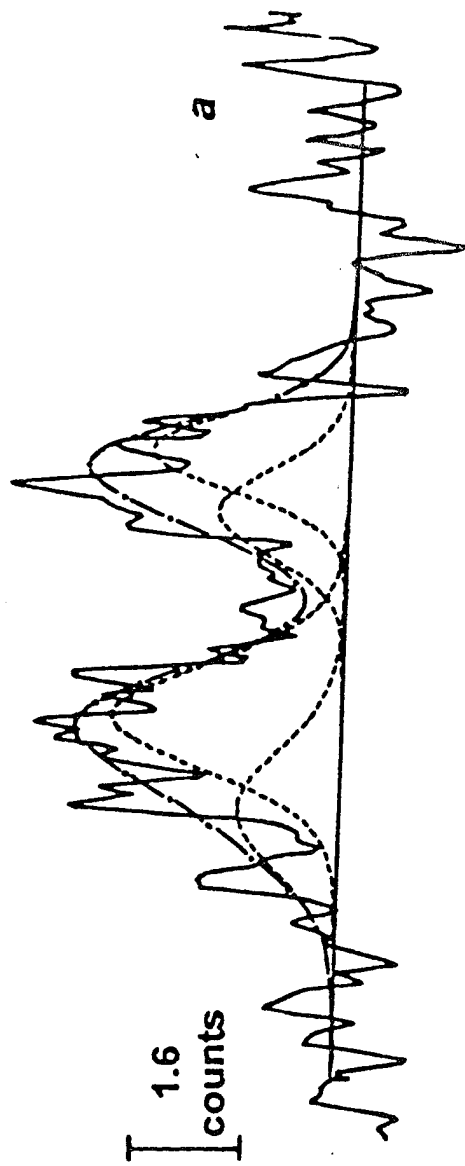


Fig. 3. Excess sulfate in Pt/C materials observed using XPS: a) Pt/C received 10% Pt/C₁₀₀₋₇₀ commercial catalyst [E-TEK] which has been synthesized from sulfate-based Pt precursors; b) 10% Pt-black/C₁₀₀₋₇₀ which has been water suspended using H₂SO₄ as a flocculant; c) VCA (vulcan carbon after two treatments of water dispersion, hot pressing, and oven heating).

Fig 7

To John Karauk
From Karauk & Visser
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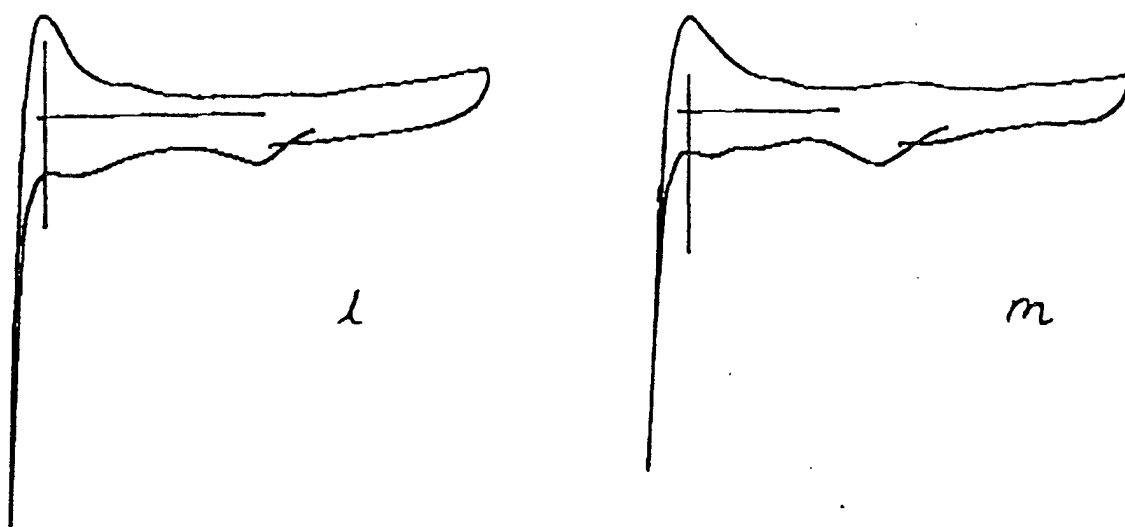


Fig 4 l 10% Pt black on desulfurized vulcan carbon,
as prepared

Fig 4 m 10% Pt black on desulfurized vulcan carbon,
heated in air to 295°C with no H_2O treatment.
(compare to fig. 4f)

F. 4