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(71) Demandeur/Applicant:
BALLARD POWER SYSTEMS INC., CA

(72) Inventeurs/Inventors:
WEZEL, REGINA, DE;
WILL, SUSANNE, DE;
MULLER, JENS, DE;
URBAN, PETER, DE;
COLBOW, KEVIN M., CA;
REYNARD, LINDA, CA

(74) Agent: RUSSELL REYNEKE

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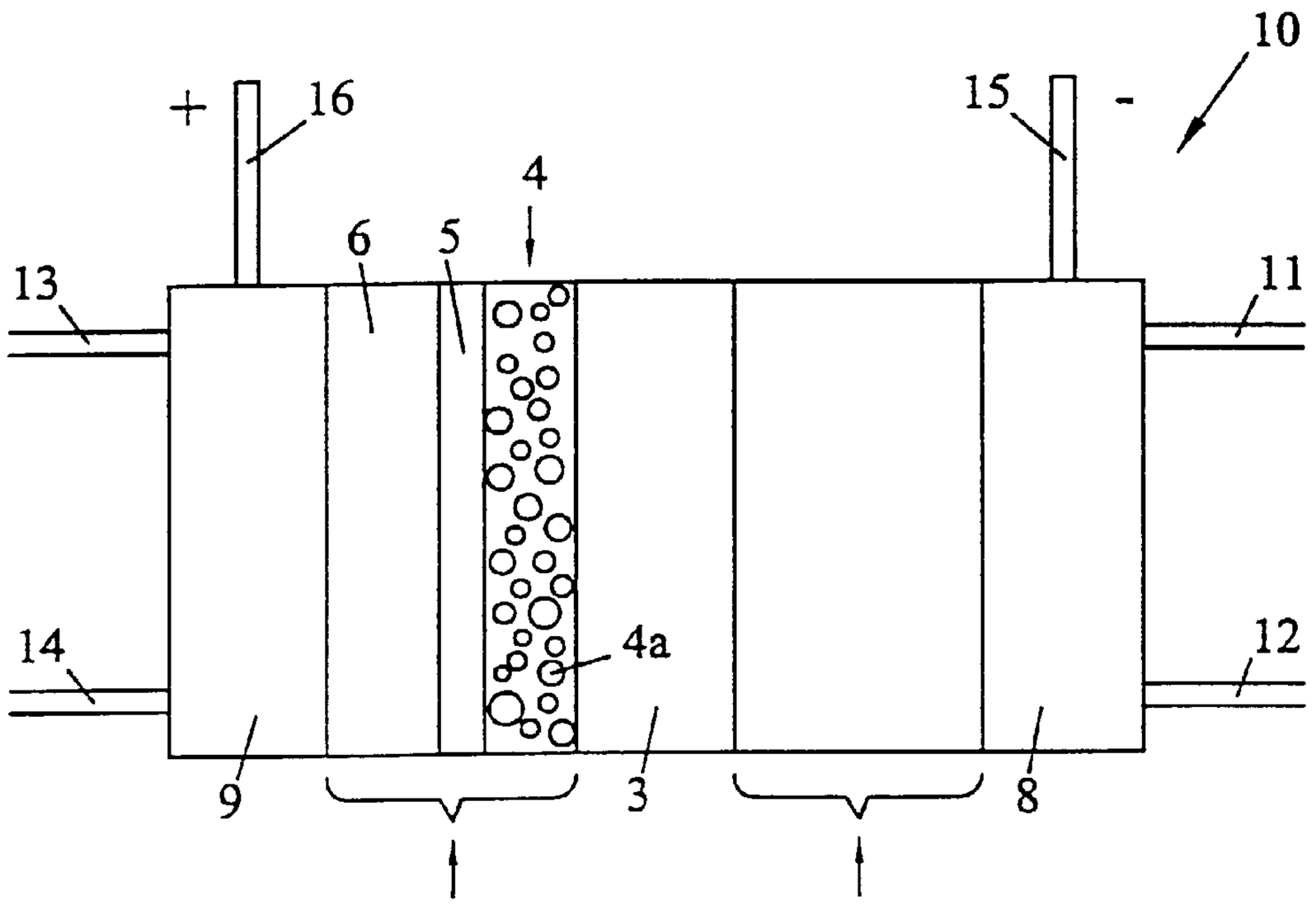
(54) Title: IMPROVED CATHODE STRUCTURES FOR DIRECT LIQUID FEED FUEL CELLS



(57) Abrégé/Abstract:
Direct liquid feed solid polymer fuel cells are supplied with a liquid fuel stream typically comprising a mixture of fuel and a substantial amount of water (for example, liquid feed direct methanol fuel cells). The oxidant stream supplied however is typically a gaseous stream (for example, air) as is commonly supplied to gas feed solid polymer fuel cells. A greater amount of water typically diffuses from the anode side to the cathode side in liquid feed cells, thereby having an effect on water management at the cathode. A different cathode structure having a lesser amount of hydrophobic additive in the cathode substrate is preferred in liquid feed fuel cells. Further, a thinner cathode may be used without sacrificing fuel cell performance, by using a combination of a thinner carbonaceous support in the cathode substrate and a carbon-based sublayer between the cathode substrate and electrocatalyst layer.

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(71) Applicant *(for all designated States except US)*: **BALLARD POWER SYSTEMS INC.** [CA/CA]; 9000 Glenlyon Parkway, Burnaby, British Columbia V5J 5J9 (CA).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **WEZEL, Regina** [DE/DE]; Virchowstr. 9, 89075 Ulm (DE). **WILL, Susanne** [DE/DE]; Bessererstr. 2, 89073 Ulm (DE). **MÜLLER, Jens** [DE/DE]; Fünf-Bäume-Weg 195, 89075 Ulm (DE). **URBAN, Peter** [DE/DE]; Eisenbergle 14, 71116 Gärtringen (DE). **COLBOW, Kevin, Michael** [CA/CA]; 1305 Fernwood Cresent, North Vancouver, British Columbia V7P 1K3 (CA). **REYNARD, Linda** [CA/CA]; 2271 Magnussen Place, North Vancouver, British Columbia V7J 3R6 (CA).

(74) Agent: **DE KOCK, Elbie, R.**; Russell Reyneke, Two Bentall Centre, Suite 700, 555 Burrard Street, Vancouver, British Columbia (CA).

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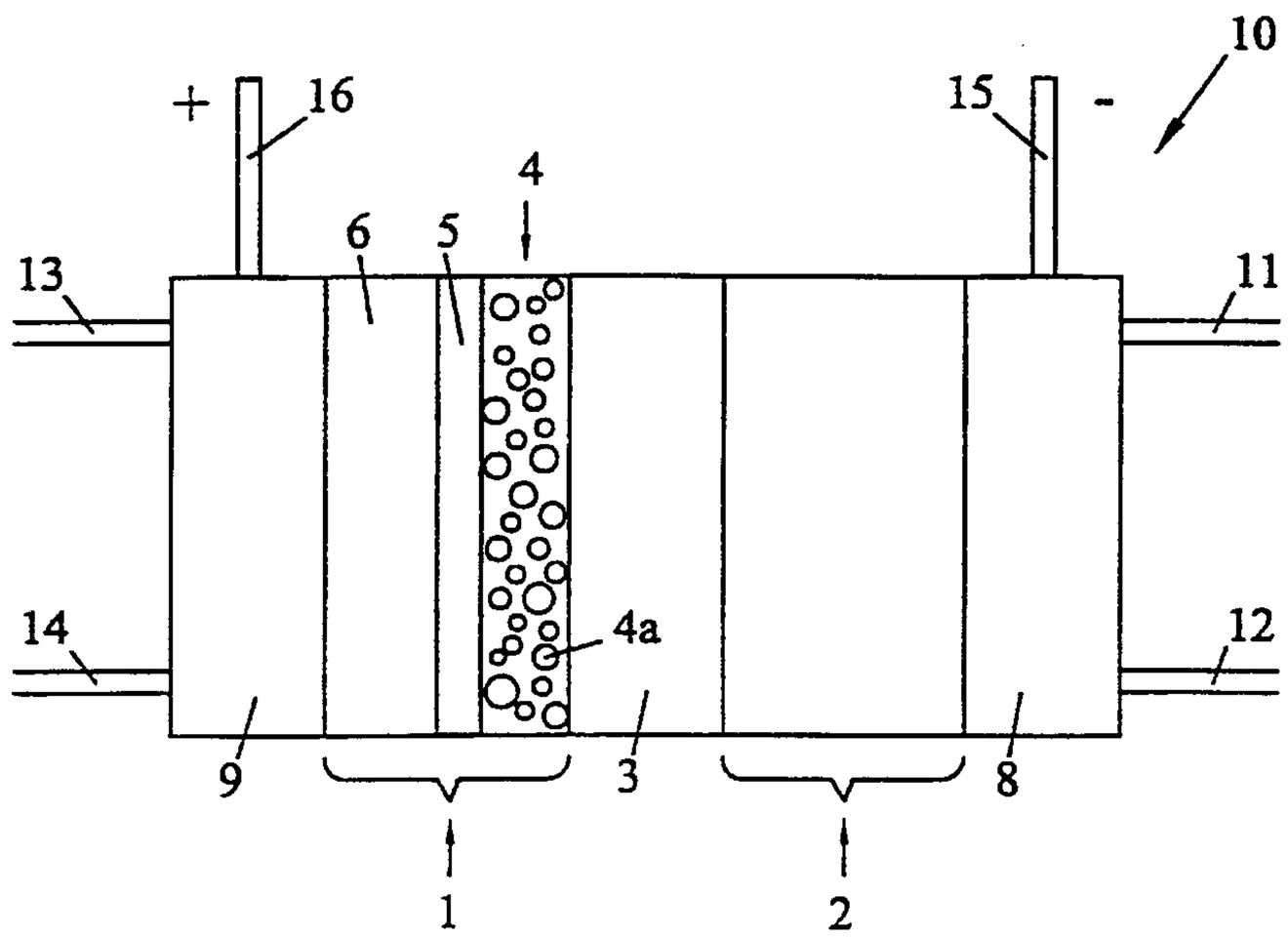
(54) Title: IMPROVED CATHODE STRUCTURES FOR DIRECT LIQUID FEED FUEL CELLS



(57) Abstract: Direct liquid feed solid polymer fuel cells are supplied with a liquid fuel stream typically comprising a mixture of fuel and a substantial amount of water (for example, liquid feed direct methanol fuel cells). The oxidant stream supplied however is typically a gaseous stream (for example, air) as is commonly supplied to gas feed solid polymer fuel cells. A greater amount of water typically diffuses from the anode side to the cathode side in liquid feed cells, thereby having an effect on water management at the cathode. A different cathode structure having a lesser amount of hydrophobic additive in the cathode substrate is preferred in liquid feed fuel cells. Further, a thinner cathode may be used without sacrificing fuel cell performance, by using a combination of a thinner carbonaceous support in the cathode substrate and a carbon-based sublayer between the cathode substrate and electrocatalyst layer.

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IMPROVED CATHODE STRUCTURES FOR DIRECT LIQUID FEED FUEL CELLS

Field Of The Invention

The present invention relates to cathode structures for solid polymer fuel cells operating directly on a liquid fuel stream in which the fuel is directly oxidized at the anode. In particular, it relates to cathode structures that provide improved performance in direct methanol fuel cells.

Background Of The Invention

Electrochemical fuel cells convert reactants, namely fuel and oxidants, to generate electric power and reaction products. Electrochemical fuel cells generally employ an electrolyte disposed between two electrodes, namely a cathode and an anode. An electrocatalyst is needed to induce the desired electrochemical reactions at the electrodes. Solid polymer fuel cells operate in a range from about 80EC to about 200EC and are particularly preferred for portable and motive applications. Solid polymer fuel cells employ a membrane electrode assembly ("MEA") which comprises a solid polymer electrolyte or ion-exchange membrane disposed between the two electrode layers. Flow field plates for directing the reactants across one surface of each electrode are generally disposed on each side of the MEA. The electrocatalyst used may be a metal black, an alloy or a supported metal catalyst, for example, platinum on carbon. The electrocatalyst is typically incorporated at the electrode/electrolyte interfaces.

A broad range of reactants have been contemplated for use in solid polymer fuel cells and such reactants may be delivered in gaseous or liquid streams. The oxidant stream may, for example, be substantially pure oxygen but preferably air, a dilute oxygen stream, is employed. The fuel stream may be substantially pure hydrogen gas, a

gaseous hydrogen-containing reformate stream derived from a suitable feedstock, or a suitable gaseous or liquid organic fuel mixture. A fuel cell operating on a liquid fuel stream in which the fuel is reacted electrochemically at the anode (directly oxidized) is known as a direct liquid feed fuel cell.

A direct methanol fuel cell (DMFC) is a type of fuel cell in which methanol is directly oxidized at the anode. Although it may be operated on aqueous methanol vapour, a DMFC generally operates in a liquid feed mode on an aqueous methanol fuel solution. There is often a problem in DMFCs with substantial crossover of methanol fuel from the anode to the cathode side through the membrane electrolyte. The methanol that crosses over may react with oxidant at the cathode and then cannot be recovered, resulting in significant fuel inefficiency and deterioration in fuel cell performance. To reduce crossover, very dilute solutions of methanol (for example about 5% methanol in water) are typically used as fuel streams in liquid feed DMFCs. A considerable crossover of water can also occur from the anode to cathode side in addition to water that is produced at the cathode as a result of the electrochemical reaction there. Because of the extra water which may be present at the cathode in a direct liquid feed fuel cell, a cathode construction providing superior performance in a gas feed solid polymer fuel cell will not necessarily give superior performance in a DMFC even if both cell types are supplied with similar oxidant streams.

Electrodes for solid polymer fuel cells generally comprise a substrate (a porous electrically conductive sheet material) and an electrocatalyst layer. The electrocatalyst layer is located so as to be adjacent the electrolyte when assembled into a MEA, and can be deposited directly on the substrate or on the membrane

electrolyte. Other materials, for example, polytetrafluoroethylene (PTFE) and proton conducting ionomer, are typically incorporated into the electrocatalyst layer for purposes of controlling wetting characteristics, providing an ionic pathway for protons to the membrane electrolyte, acting as a binder, and the like. The electrode substrate serves to distribute fluids (for example, reactants and/or reaction products such as water product at the cathode or carbon dioxide product at a DMFC anode) from a flow field passage to an associated electrocatalyst layer or vice versa. Electrode substrates may be made, for example, of porous carbon cloth or paper. As with the electrocatalyst layer, other materials, such as PTFE and proton conducting ionomer, may be incorporated into the substrate for similar purposes. For volumetric energy density, the use of thinner electrodes and hence MEAs is preferred.

A range of cathode constructions have been used in gaseous oxidant feed solid polymer fuel cells. Prior art cathodes comprising carbonaceous substrates typically contain a significant amount of a hydrophobic additive (for example, >10% by weight PTFE) and typically exceed about 230 micrometers in thickness for purposes of improved oxidant distribution and product water management.

Summary Of The Invention

Preferred cathode constructions for liquid feed solid polymer fuel cells operating on liquid aqueous fuel streams differ from those of gaseous feed solid polymer fuel cells. Unexpectedly, the use of less hydrophobic additive in the cathode may be advantageous to fuel cell performance. Further, thinner cathodes comprising a porous carbonaceous support less than 230 micrometers thick, and a carbon-based sublayer between the substrate

and the electrocatalyst layer may be employed to provide similar or better performance, and thus are advantageous with regards to volumetric energy density of the fuel cell.

An improved direct liquid feed solid polymer fuel cell comprises a cathode, an anode, and a solid polymer electrolyte. The cathode is supplied with a gaseous oxidant stream and the anode is supplied with a liquid fuel stream comprising fuel and water wherein the fuel is directly oxidized at the anode. The cathode of the improved fuel cell comprises a substrate and an electrocatalyst layer. The substrate comprises a carbonaceous support and a first hydrophobic additive. In one embodiment the amount of the first hydrophobic additive in the cathode substrate is less than 10% by weight. In another embodiment, the thickness of the carbonaceous support in the cathode substrate is less than 230 micrometers and there is a carbon-based sublayer in the cathode between the substrate and the electrocatalyst layer. The embodiments can be combined.

The first hydrophobic additive may be PTFE. In particular, the amount of the PTFE in the cathode substrate may be about 6% by weight.

The thickness of the carbonaceous support in the cathode substrate may be less than 230 micrometers and greater than 75 micrometers. In particular, the thickness of the carbonaceous support in the cathode substrate may be about 150 micrometers. The loading of the carbon-based sublayer may be less than about 0.7 mg/cm^2. The thickness of the carbon-based sublayer above the substrate may be less than about 25 micrometers.

The carbon-based sublayer may comprise a second hydrophobic additive. The second hydrophobic additive may also be PTFE and may be present in an amount of from about 6% to 30% by weight of the sublayer. The preferred amount

of the second hydrophobic additive may depend on the manner in which the electrocatalyst layer is applied to the cathode substrate. For instance, a larger amount (for example, about 30%) may be preferred if the electrocatalyst layer is manually applied while a smaller amount (for example, about 6%) may be preferred if the electrocatalyst layer is applied by a spraying method.

The electrocatalyst layer in the cathode comprises electrocatalyst and also may comprise a third hydrophobic additive. The third hydrophobic additive may also be PTFE and may be present in an amount of about 6% by weight of the electrocatalyst layer.

Use of less than 10% by weight of the first hydrophobic additive in the cathode substrate can result in significant improvement in the performance of liquid feed fuel cells in which the fuel stream comprises a substantial amount of water (for example, typical DMFCs). Use of a sublayer and a carbonaceous support less than 230 micrometers thick can provide a thinner cathode structure with similar or better fuel cell performance.

Brief Description Of The Drawings

FIG. 1 is a schematic diagram of a direct methanol solid polymer fuel cell.

FIG. 2a shows plots of output voltage as a function of current density for the direct methanol fuel cells (DMFCs) in the Examples whose cathodes comprise carbon substrates with different amounts of PTFE.

FIG. 2b shows the output voltages at constant current of the DMFCs shown in FIG. 2a, as a function of the oxidant stoichiometry.

FIG. 3a shows plots of output voltage as a function of current density for DMFCs in the Examples whose cathodes comprise carbon substrates of differing thickness and/or which also comprise a carbon-based sublayer.

FIG. 3b shows the output voltages at constant current for the DMFCs shown in FIG. 3a, as a function of the oxidant stoichiometry.

FIG. 4a shows plots of output voltage as a function of current density for DMFCs in the Examples whose cathodes comprise carbon-based sublayers with different amounts of PTFE and whose electrocatalyst layers were applied in different ways.

FIG. 4b shows the output voltages at constant current for the DMFCs shown in FIG. 4a, as a function of the oxygen stoichiometry.

Detailed Description Of Preferred Embodiments

The improved cathode structures described herein are suitable for use in fuel cells in which the supplied liquid fuel stream comprises substantially more water than typical gas feed fuel streams (that is, more than humidified hydrogen or methanol/water vapor fuel streams). For instance, the improved cathode structures are suitable for use in liquid feed fuel cells such as liquid feed direct methanol fuel cells (DMFCs). The liquid fuel stream in a DMFC comprises at least the same number of moles of water as methanol (since the anode reaction requires one mole of water for each mole of methanol). In fact, typically dilute solutions of methanol in water are employed in order to reduce crossover of methanol from the anode to cathode.

FIG. 1 shows a schematic diagram of a liquid feed DMFC comprising an improved cathode structure. For purposes of illustration, a preferred series stack of fuel cells is represented merely by a single liquid feed fuel cell 10 in FIG. 1. Fuel cell 10 contains a membrane electrode assembly (MEA) comprising a porous cathode 1 and porous anode 2 that are bonded to a solid polymer membrane electrolyte 3. Liquid fuel flow field 8 and oxidant flow

field 9 are pressed against anode 2 and cathode 6 respectively on the faces opposite the membrane electrolyte 3. Fuel cell 10 has a liquid fuel stream inlet 11, a liquid fuel stream outlet 12, an oxidant inlet 13, and an oxidant outlet 14. Electrical power is obtained from the fuel cell via negative and positive terminals 15 and 16 respectively.

As shown, cathode 1 comprises an electrocatalyst layer 4, a carbonaceous substrate 6, and a carbon-based sublayer 5 between electrocatalyst layer 4 and substrate 6. Each of electrocatalyst layer 4, substrate 6, and sublayer 5 comprises an amount of a suitable hydrophobic additive (for example, PTFE). Electrocatalyst layer 4 also comprises proton conducting ionomer dispersed throughout (for example, NAFION™). The hydrophobic additive serves to modify the wetting characteristics of each component and may also serve as a binder. The ionomer provides ionic pathways from electrocatalyst particles 4a in layer 4 to membrane electrolyte 3.

Cathode 1 further comprises several features leading to improved fuel cell performance in liquid feed fuel cells. Substrate 6 preferably comprises less than 10% by weight PTFE additive and is therefore more hydrophilic than substrates with more PTFE. The combination of the carbonaceous support in substrate 6 (preferably less than about 230 micrometers thick) and the carbon-based sublayer (preferably less than about 0.7 mg/cm^2 and 25 micrometers thick) provides a shorter path for water removal than thicker substrates. While these features might be expected to adversely affect the distribution of oxidant to the cathode electrocatalyst, it has been found that a net performance improvement can be realized nonetheless. (Like electrocatalyst layer 4, the carbon-based sublayer 5 is very thin relative to substrate 6 and is thus generally

not so significant compared to the thickness of the substrate.)

Without being bound by any particular theory, the observed performance improvements are believed to relate to the substantial diffusion of water across the membrane electrolyte in such liquid feed fuel cells, which significantly alters the water management situation at the cathode. For instance, in certain DMFC embodiments, water crossover from the anode may account for up to 90% of the water at the cathode. In such cases, it seems to be relatively more important to get the water out of the cathode electrocatalyst layer than it is to get distributed oxidant in. It is generally easier to move water away from the electrocatalyst layer through a thinner substrate, although the trade-off may be poorer distribution of the oxidant to the electrocatalyst layer. Further, it is easier to move water through a substrate that is more hydrophilic (for example, has less hydrophobic additive) although again this tends to make it harder to distribute gaseous oxidant to the cathode electrocatalyst.

The following DMFC examples have been included to illustrate different embodiments and aspects of the present cathode structures, but these should not be construed as limiting in any way. For instance, the improved cathode structures described may also be used in liquid feed fuel cells operating on liquid fuel mixtures comprising a substantial amount of water and another fuel such as, for example, ethanol, dimethyl ether.

Examples

Experimental DMFCs were assembled using various modified cathode structures and were then subjected to fuel cell performance tests. Modifications to the cathode

included: varying the amount of PTFE in the cathode substrate, varying the thickness of the cathode substrate, incorporating a carbon-based sublayer in the cathode, varying the amount of PTFE in the sublayer, and varying the method of application of the electrocatalyst layer.

In a first series of fuel cells, denoted A to I, the membrane electrolyte employed in each cell was NAFION™ 117. The active area of the electrodes was about 49 cm^2. The anodes comprised electrocatalyst layers comprising unsupported platinum/ruthenium (at about 4 mg/cm^2 loading) and NAFION™ ionomer (at about 0.4 m g/cm^2 loading). The anode electrocatalyst layers were manually applied on 229 micrometer thick TGP grade (product from Toray) carbon fibre paper substrates in slurry form and were then impregnated afterwards with the ionomer. The cathodes comprised electrocatalyst layers consisting of unsupported platinum (also at about 4 mg/cm^2 loading) and 6% by weight PTFE. The cathode electrocatalyst layers were also manually applied in slurry form onto TGP grade (product from Toray) carbon fibre paper substrates. Different thicknesses of carbon fibre paper were used as cathode substrates, however, and the substrates were also impregnated with varying amounts of PTFE additive. Further, some cathodes also employed a carbon-based sublayer between the carbon fibre paper substrate and the electrocatalyst layer. The details of the cathode structures employed for each cell of this first series are summarized in Table 1 below.

Table 1

Cell	% wt. of PTFE in substrate	Nominal thickness of substrate (in micrometers)	Sublayer incorporated at cathode?
A	3.7%	152	Yes
B	6.4%	152	Yes
C	12.5%	152	Yes
D	19.7%	152	Yes
E	11.7%	229	No
F	11.8%	229	Yes
G	12.3%	152	No
H	13.2%	76	Yes
I	13.2%	152*	Yes

* This 152 micrometer substrate was prepared by stacking two pieces of 76 micrometer PTFE-impregnated carbon fibre paper together.

PTFE was introduced into the carbon fibre paper substrates by impregnation with an appropriate aqueous PTFE suspension followed by drying. Where applicable, approximately 0.46 mg/cm^2 loading of a sublayer containing carbon black and 26% wt. PTFE was applied by screen printing a carbon-based slurry onto the appropriate substrate and then drying the substrate. (Sublayer loadings less than about 0.7 mg/cm^2 have been found to be advantageous. Greater amounts may be detrimental.) The slurry consisted of polyethylene glycol (liquid), polycarbonate (liquid), Shawinigan carbon black (Chevron Chemical C50 grade), and PTFE (60% by weight PTFE in a dilute water suspension) in a weight ratio of about

33.3/20.1/2.28/0.81. The applied sublayer penetrated the pores of the carbon fibre paper typically to a depth of about 35 micrometers (as observed under a scanning electron microscope). Some sublayer material remained above the surface of the carbon fibre paper, typically with a thickness of about 10 micrometers.

The performance characteristics determined for these experimental DMFCs included output voltage versus current density (at constant fuel flow rate and constant oxidant stoichiometry except, in the case of the latter, at the lowest current densities where there may be substantial competition for the available oxygen at the cathode for methanol oxidation from methanol crossover) and output voltage versus oxidant stoichiometry (at constant current density). Stoichiometry is defined as the ratio of reactant supplied to the fuel cell to reactant consumed in the electrochemical reactions in the fuel cell. This testing was done at about 97EC. Compressed air was used as the oxidant stream and 0.45M aqueous methanol was used as the liquid fuel stream, both at 3 bar absolute pressure. In the determination of output voltage versus current density, the fluid flow rates were such that, at current densities of 300 mA/cm^2, the oxidant and fuel stoichiometries were 2 and 3 respectively. In the determination of output voltage versus oxidant stoichiometry, the same fuel stoichiometry was used and voltage was determined as a function of oxidant stoichiometry at a constant 200 mA/cm^2 current density.

FIG. 2a shows the output voltage versus current density plots for DMFCs A, B, C, and D. These fuel cells have similar cathodes except for the amount of PTFE in the carbon substrate. Fuel cell D, with the highest PTFE content in the cathode substrate, performed significantly worse than the other cells. FIG. 2b shows the output voltage versus oxidant stoichiometry plots for the same

cells. Here, the ability to maintain a high output voltage at lower oxidant stoichiometry is indicative of better performance. Again, fuel cell D, with the highest PTFE content in the substrate, performed significantly worse than the other cells. Fuel cell C, with 6.4% PTFE in the substrate, shows the best performance in both figures. (Note that some hysteresis is observed in the plots in FIG. 2b and in later FIGs. 3b and 4b. The oxidant stoichiometry is first decreased stepwise until the output voltage drops significantly. The oxidant stoichiometry is then increased stepwise until the output voltage recovers. In general, the output voltage is higher during the increase in stoichiometry than it is during the decrease in stoichiometry. This hysteresis may result from the cathode getting wetter as the stoichiometry decreases, with the possible formation of new water pathways from water deposits in the cathode. The presence of new water pathways may then improve water removal once the oxidant stoichiometry is increased again. Furthermore, the cathode potential changes when the oxidant stoichiometry is varied in this way. A change in the cathode potential can result in the removal of strongly bound adsorbates from the cathode electrocatalyst, and hence a refreshing of the cathode electrocatalyst.)

FIGs. 3a and 3b show the output voltage versus current density plots and the output voltage versus oxidant stoichiometry plots for DMFCs C and E to I inclusive. These fuel cells have roughly the same amount of PTFE in the cathode substrate but differ in cathode substrate thickness and/or presence of a sublayer at the cathode. Cells C and I show similar or better performance to that of cell E (which is a conventional cathode) although the overall thickness of the cathodes in cells C and I is about 67 micrometers thinner than that of cell E.

FIGs. 3a and 3b also show a marked improvement in performance with the use of a sublayer in cells with a 152 micrometer thick cathode substrate (comparing cells C and I to cell G which has no sublayer).

In a second series of fuel cells, denoted J, K, and L, the membrane electrolyte employed in each cell was NAFION™ 115. The electrodes were similar to those of cells A to I except that each cathode had a 0.6 mg/cm^2 carbon-based sublayer having different amounts of PTFE and each had NAFION™ ionomer in the electrocatalyst layer (at about 0.6 mg/cm^2 loading). In the cathode of cell J, the sublayer was applied using a spray technique which results in somewhat more sublayer material remaining above the surface of the substrate. The thickness of the sprayed sublayer above the carbon fibre paper surface as observed under a scanning electron microscope was about 22 micrometers thick on average (actual range from about 15 to 25 micrometers thick). Further, each cathode substrate was 229 micrometers thick and contained about 6% by wt. PTFE. Finally, in some cathodes, the electrocatalyst layer was applied using a spray technique. Table 2 below summarizes the differences between these cells.

Table 2

Cell	% wt. of PTFE in sublayer	Method of application of electrocatalyst layer
J	6%	Spray
K	30%	Spray
L	30%	Manual

The performance characteristics were determined as above except that testing here was done at 110EC and 0.4M aqueous methanol was used as the fuel stream. Also, in this series, the performance characteristics were determined at constant fuel stoichiometry.

FIGs. 4a and 4b show the output voltage versus current density plots and the output voltage versus oxidant stoichiometry plots for DMFCs J, K, and L. The performance of cell K is substantially worse than the other two, indicating that the preferred amount of PTFE in the sublayer may depend on the manner in which the electrocatalyst layer is applied to the cathode substrate.

While particular elements, embodiments and applications of the present invention have been shown and described, it will be understood, of course, that the invention is not limited thereto since modifications may be made by those skilled in the art without departing from the spirit and scope of the present disclosure, particularly in light of the foregoing teachings.

What is claimed is:

1. An improved liquid feed solid polymer fuel cell comprising a cathode, an anode, and a solid polymer electrolyte, said cathode supplied with a gaseous oxidant stream, said anode supplied with a liquid fuel stream comprising fuel and water wherein said fuel is directly oxidized at said anode, said cathode comprising a substrate and an electrocatalyst layer, and said substrate comprising a porous carbonaceous support and a first hydrophobic additive, wherein the improvement comprises at least one of the group consisting of:

(a) an amount of said first hydrophobic additive in said cathode substrate less than 10% by weight; and

(b) a thickness of said carbonaceous support in said cathode substrate less than 230 micrometers and

(c) a carbon-based sublayer in said cathode between said substrate and said electrocatalyst layer.

2. The improved liquid feed solid polymer fuel cell of claim 1 wherein said amount of said first hydrophobic additive in said cathode substrate is less than 10% by weight and said first hydrophobic additive is polytetrafluoroethylene.

3. The improved liquid feed solid polymer fuel cell of claim 2 wherein said amount of said first hydrophobic additive in said cathode substrate is about 6% by weight.

4. The improved liquid feed solid polymer fuel cell of claim 2 wherein said amount of said first hydrophobic additive in said cathode substrate is about 6% by weight.

5. The improved liquid feed solid polymer fuel cell of claim 4 wherein said thickness of said carbonaceous support in said cathode substrate is about 150 micrometers.

6. The improved liquid feed solid polymer fuel cell of claim 1 comprising said carbon-based sublayer in said cathode between said substrate and said electrocatalyst layer wherein the loading of said carbon-based sublayer is less than about 0.7 mg/cm^2.

7. The improved liquid feed solid polymer fuel cell of claim 1 comprising said carbon-based sublayer in said cathode between said substrate and said electrocatalyst layer wherein said carbon-based sublayer is less than about 25 micrometers thick.

8. The improved liquid feed solid polymer fuel cell of claim 1 comprising said carbon-based sublayer in said cathode between said substrate and said electrocatalyst layer wherein said carbon-based sublayer comprises a second hydrophobic additive.

9. The improved liquid feed solid polymer fuel cell of claim 8 wherein said second hydrophobic additive is polytetrafluoroethylene.

10. The improved liquid feed solid polymer fuel cell of claim 9 wherein the amount of said second hydrophobic additive in said sublayer is from about 6% to 30% by weight.

11. The improved liquid feed solid polymer fuel cell of claim 1 wherein said electrocatalyst layer comprises electrocatalyst and a third hydrophobic additive.

12. The improved liquid feed solid polymer fuel cell of claim 11 wherein said third hydrophobic additive is polytetrafluoroethylene.

13. The improved liquid feed solid polymer fuel cell of claim 12 wherein the amount of said third hydrophobic additive in said electrocatalyst layer is about 6% by weight.

14. The improved liquid feed solid polymer fuel cell of claim 1 wherein said fuel is methanol.

15. A method of improving the performance of a liquid feed solid polymer fuel cell comprising a cathode, an anode, and a solid polymer electrolyte, said cathode supplied with a gaseous oxidant stream, said anode supplied with a liquid fuel stream comprising fuel and water wherein said fuel is directly oxidized at said anode, said cathode comprising a substrate and an electrocatalyst layer, and said substrate comprising a porous carbonaceous support and a first hydrophobic additive, said method comprising at least one of the steps in the group consisting of:

(a) incorporating less than 10% by weight of a first hydrophobic additive in said cathode substrate;

(b) employing a thickness of said carbonaceous support in said cathode substrate less than 230 micrometers; and

(c) employing a carbon-based sublayer in said cathode between said substrate and said electrocatalyst layer.

16. The method of claim 15 comprising using less than 10% by weight of said first hydrophobic additive in

said cathode substrate wherein said first hydrophobic additive is polytetrafluoroethylene.

17. The method of claim 16 comprising using about 6% by weight of said first hydrophobic additive in said cathode substrate.

18. The method of claim 15 wherein said thickness of said carbonaceous support in said cathode substrate is less than 230 micrometers and greater than 75 micrometers.

19. The method of claim 18 wherein said thickness of said carbonaceous support in said cathode substrate is about 150 micrometers.

20. The method of claim 18 wherein said thickness of said carbonaceous support in said cathode substrate is about 150 micrometers.

21. The method of claim 15 wherein said cathode comprises said carbon-based sublayer and said carbon-based sublayer is less than about 25 micrometers thick.

22. The method of claim 15 wherein said cathode comprises said carbon-based sublayer and said carbon-based sublayer comprises a second hydrophobic additive.

23. The method of claim 22 wherein said second hydrophobic additive is polytetrafluoroethylene.

24. The method of claim 23 comprising using about 6% by weight of said second hydrophobic additive in said sublayer.

25. The method of claim 24 comprising spraying said electrocatalyst layer onto said sublayer.

26. The method of claim 22 comprising using about 30% by weight of said second hydrophobic additive in said sublayer.

27. The method of claim 26 comprising manually applying said electrocatalyst layer onto said sublayer.

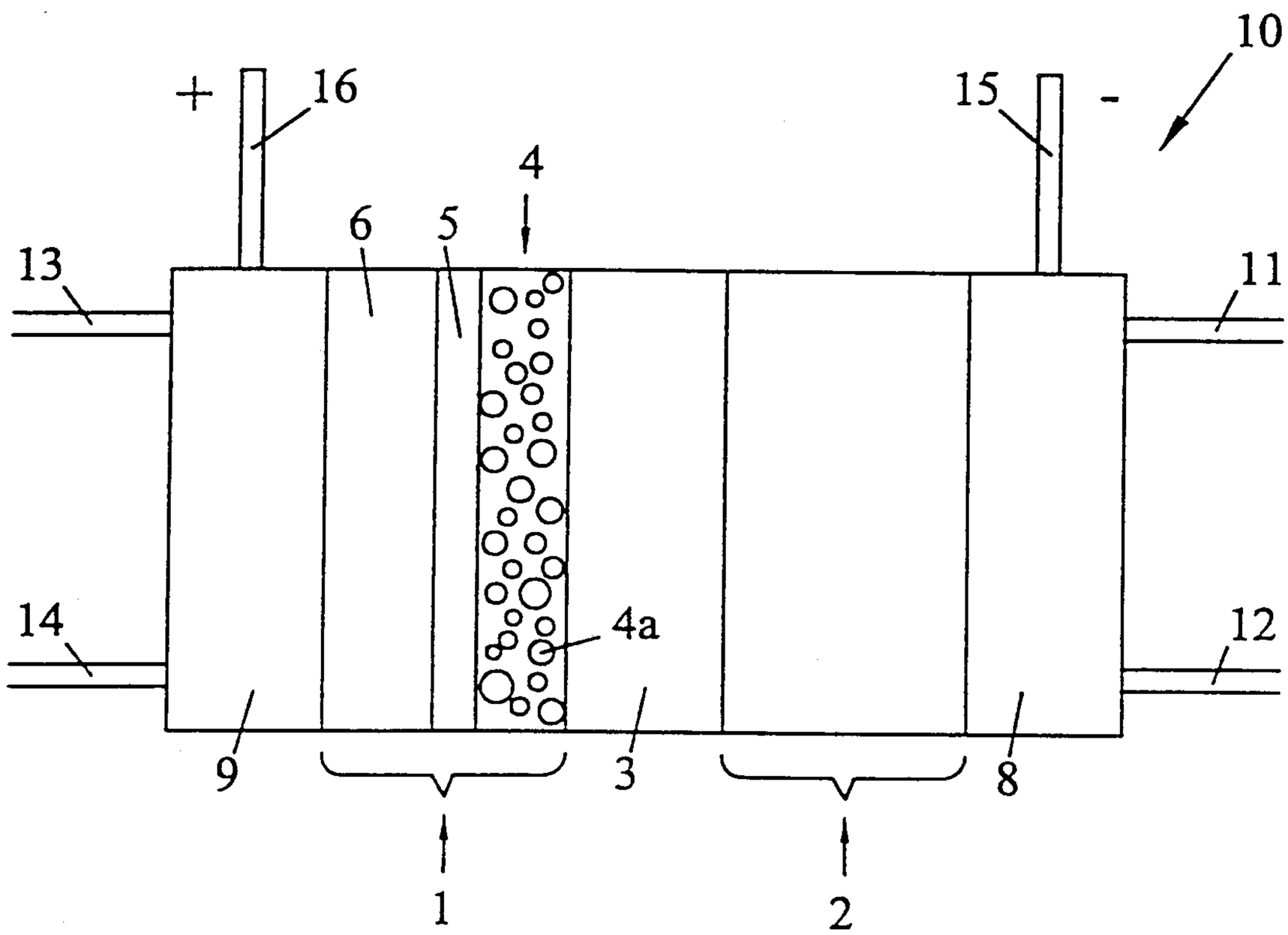


FIG. 1

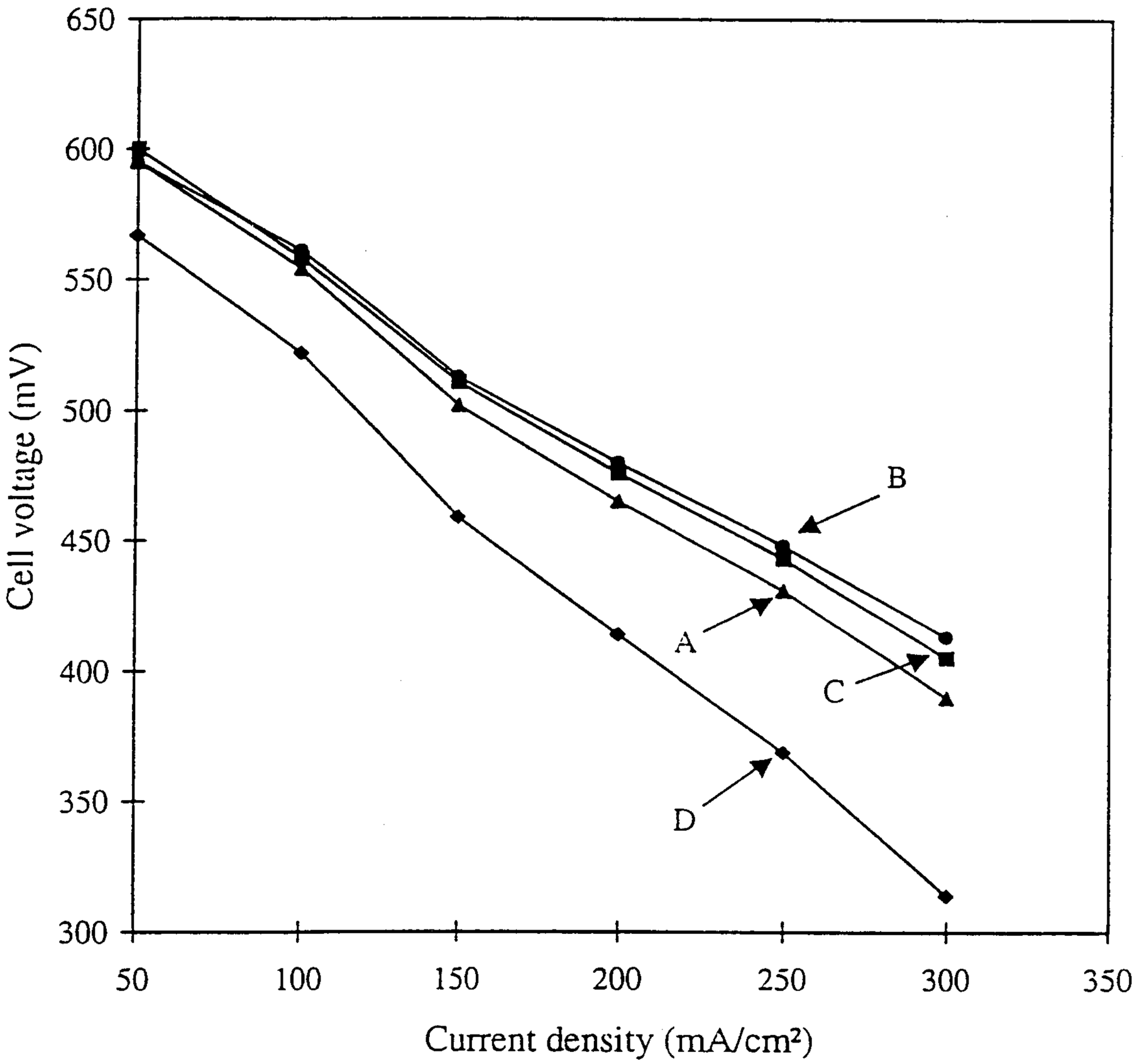

650
600
550
500
450
400
350
300
Cell voltage (mV)
50
100
150
200
250
300
350
Current density (mA/cm²)
A
B
C
D

FIG. 2a

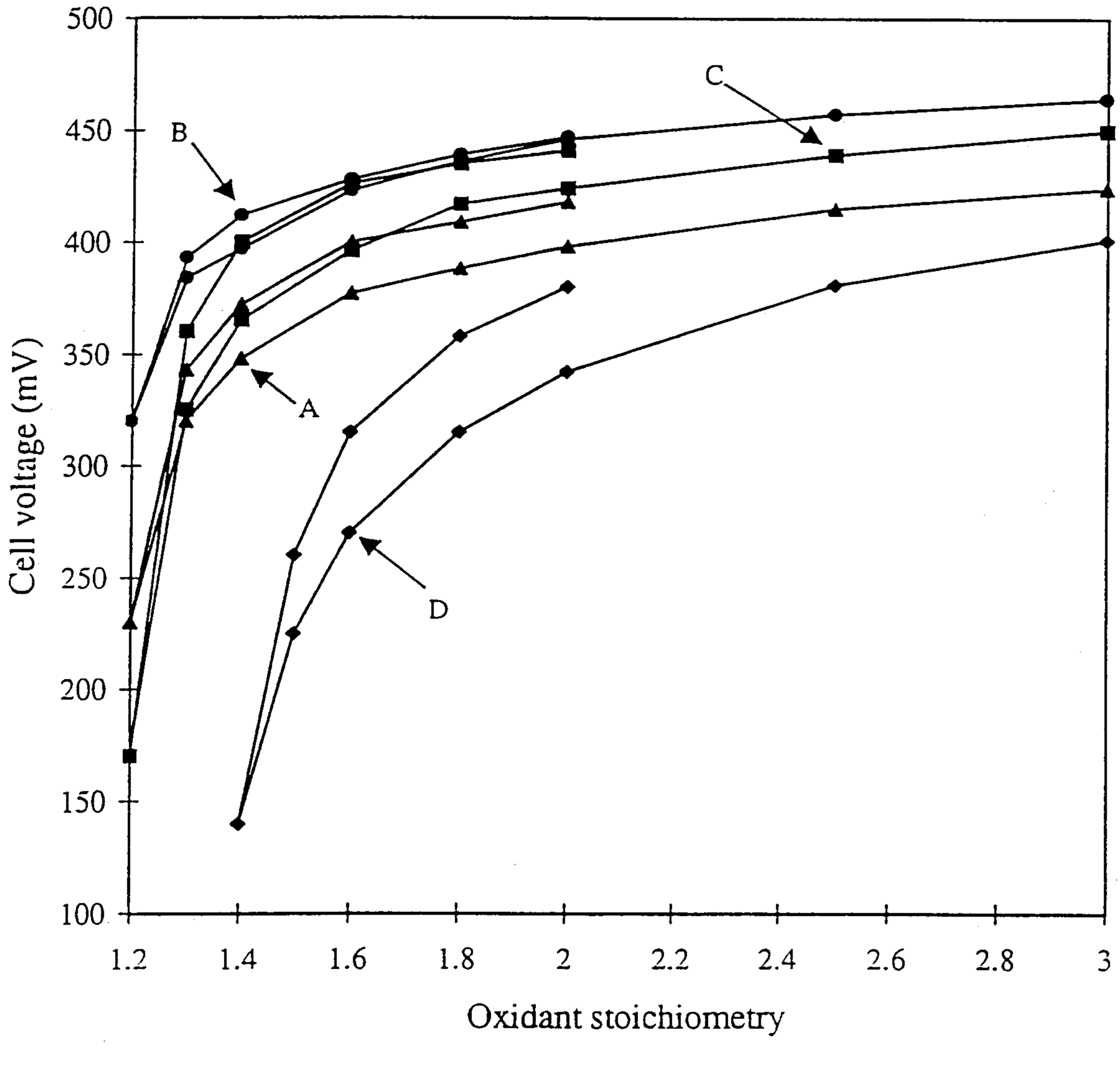

500
450
400
350
300
250
200
150
100
Cell voltage (mV)
A
B
C
D
1.2
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
3
Oxidant stoichiometry

FIG. 2b

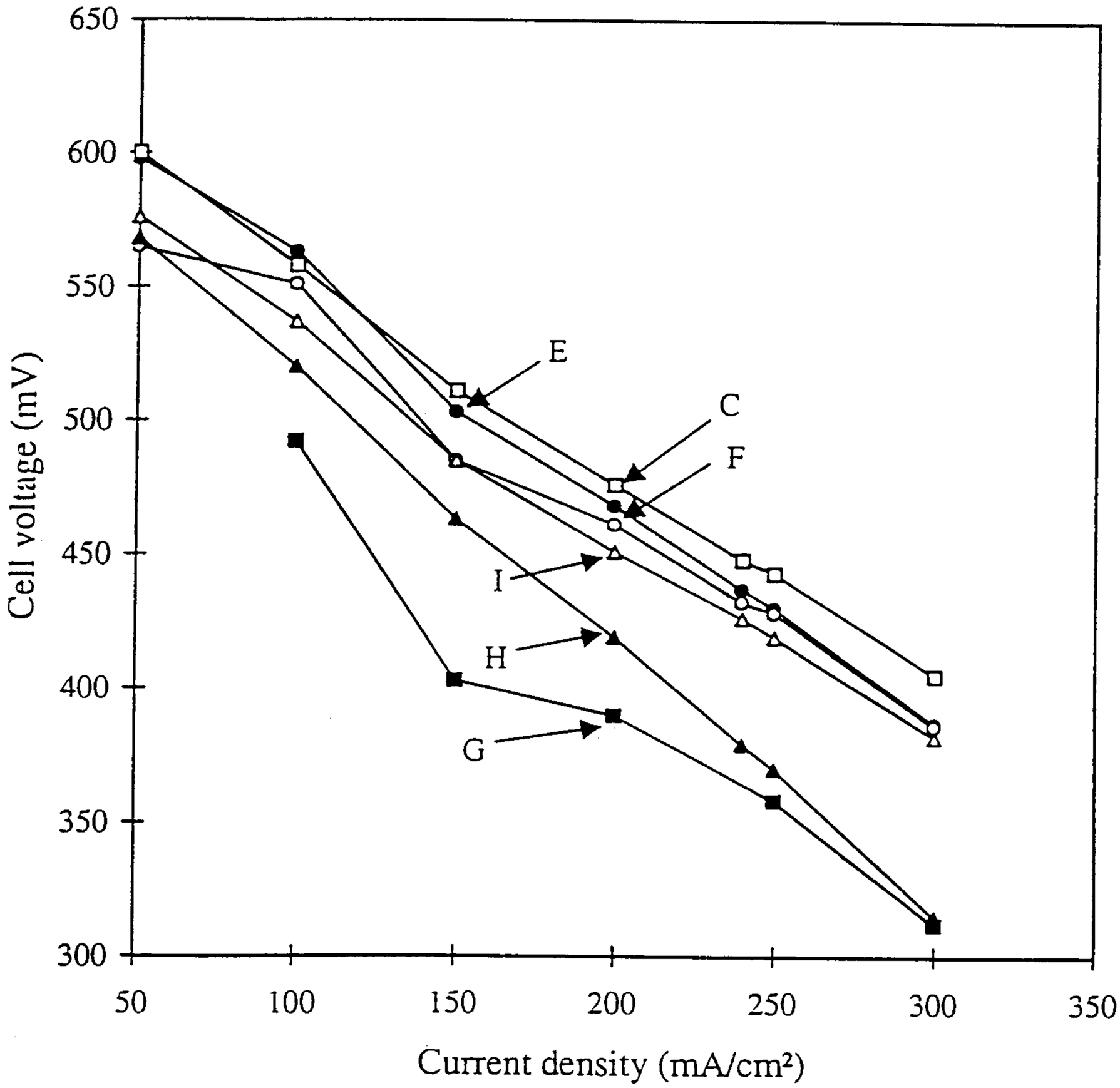

650
600
550
500
450
400
350
300
Cell voltage (mV)
50
100
150
200
250
300
350
Current density (mA/cm²)
E
C
F
I
H
G

FIG. 3a

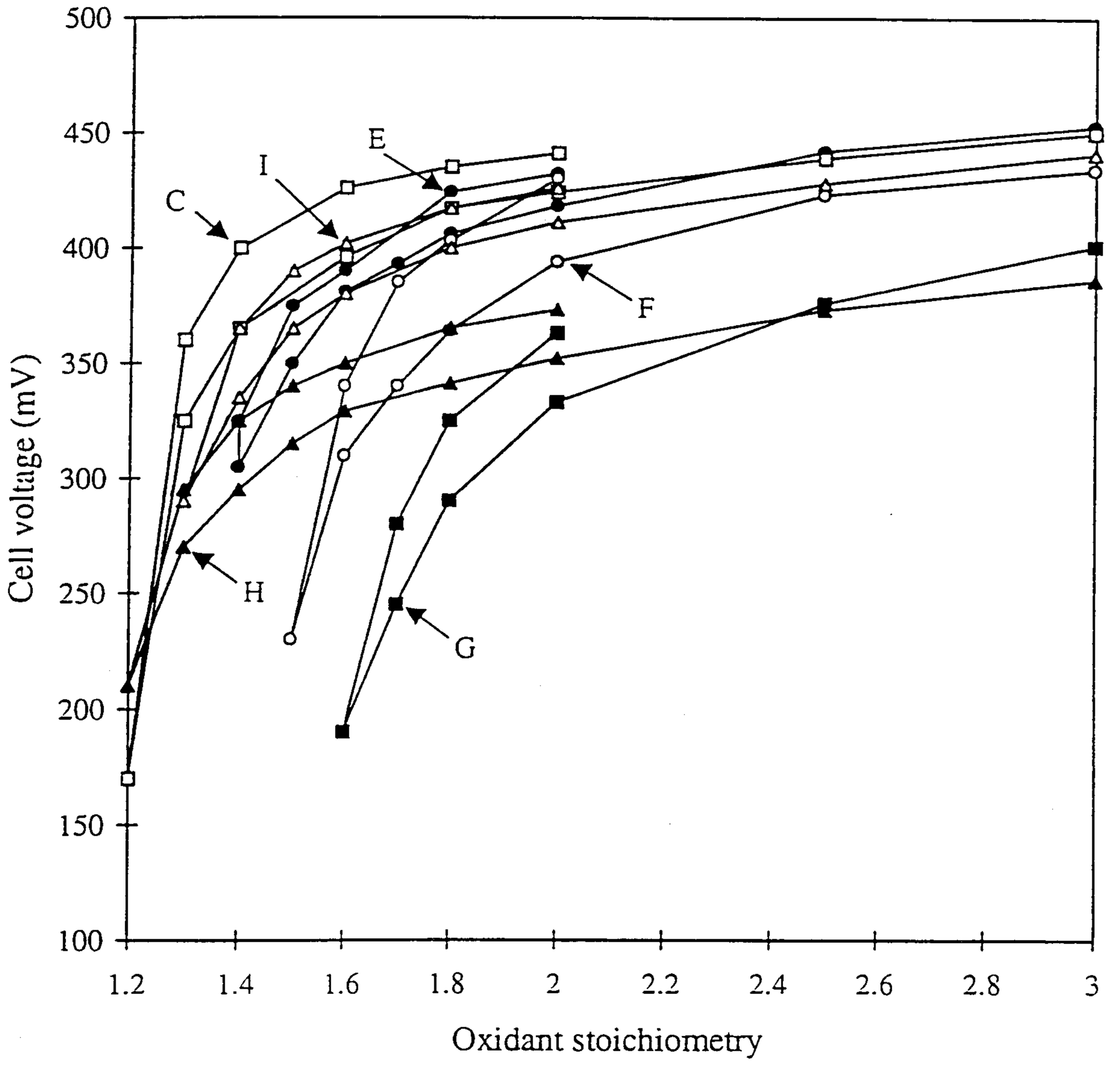

500
450
400
350
300
250
200
150
100
Cell voltage (mV)
1.2
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
3
Oxidant stoichiometry
C
I
E
F
H
G

FIG. 3b

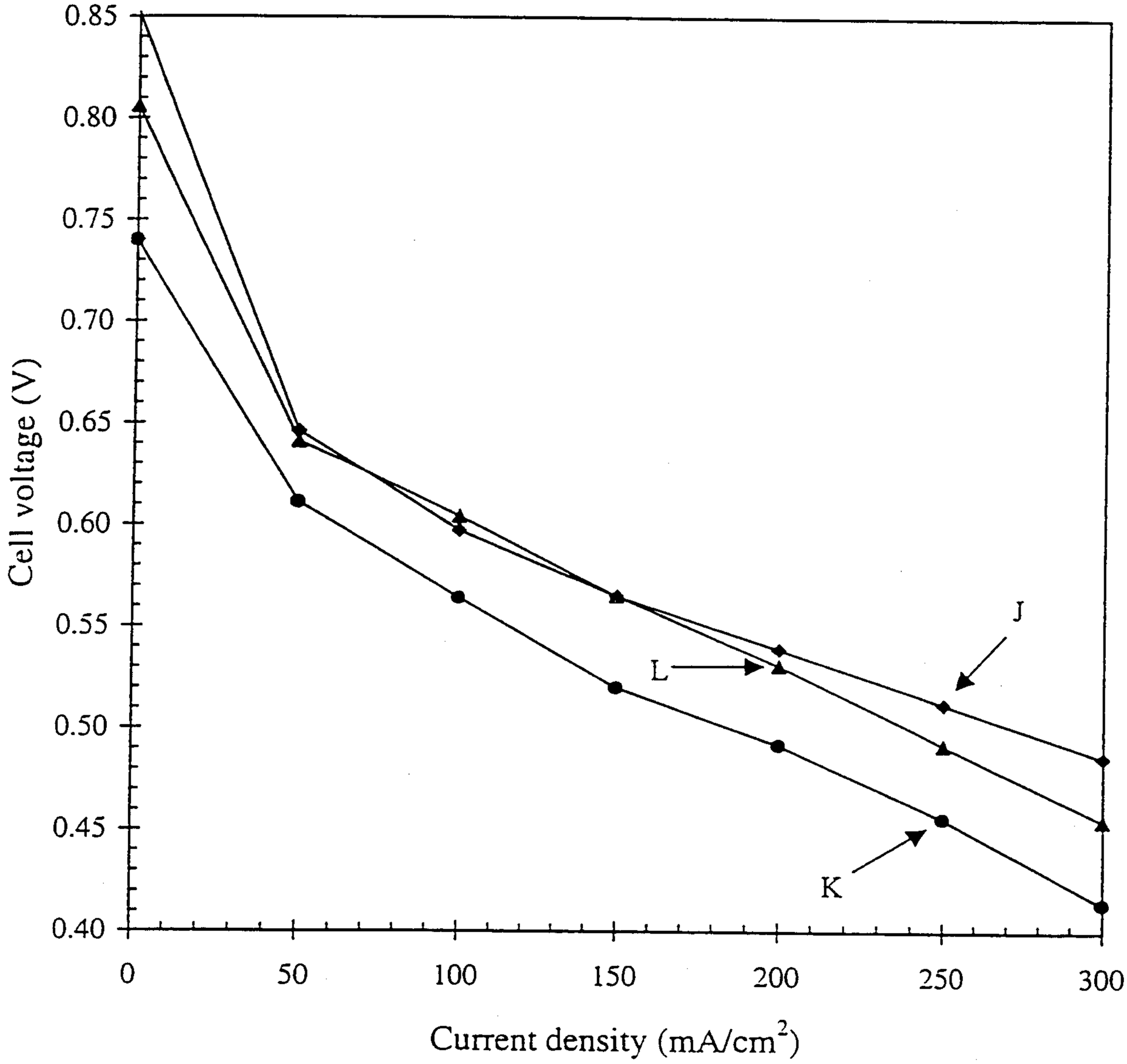

0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
Cell voltage (V)
0
50
100
150
200
250
300
Current density (mA/cm^2)
J
L
K

FIG. 4a

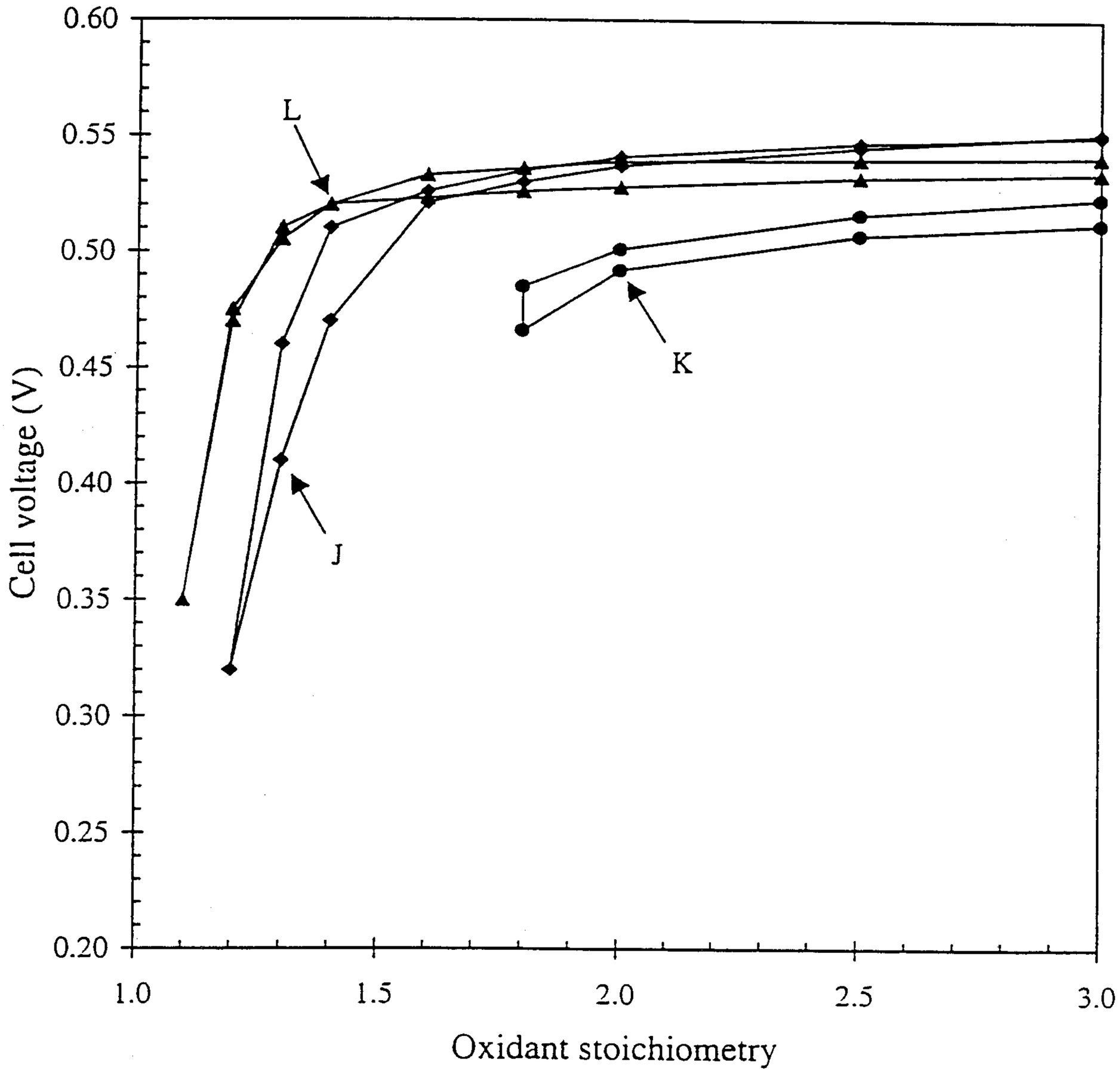
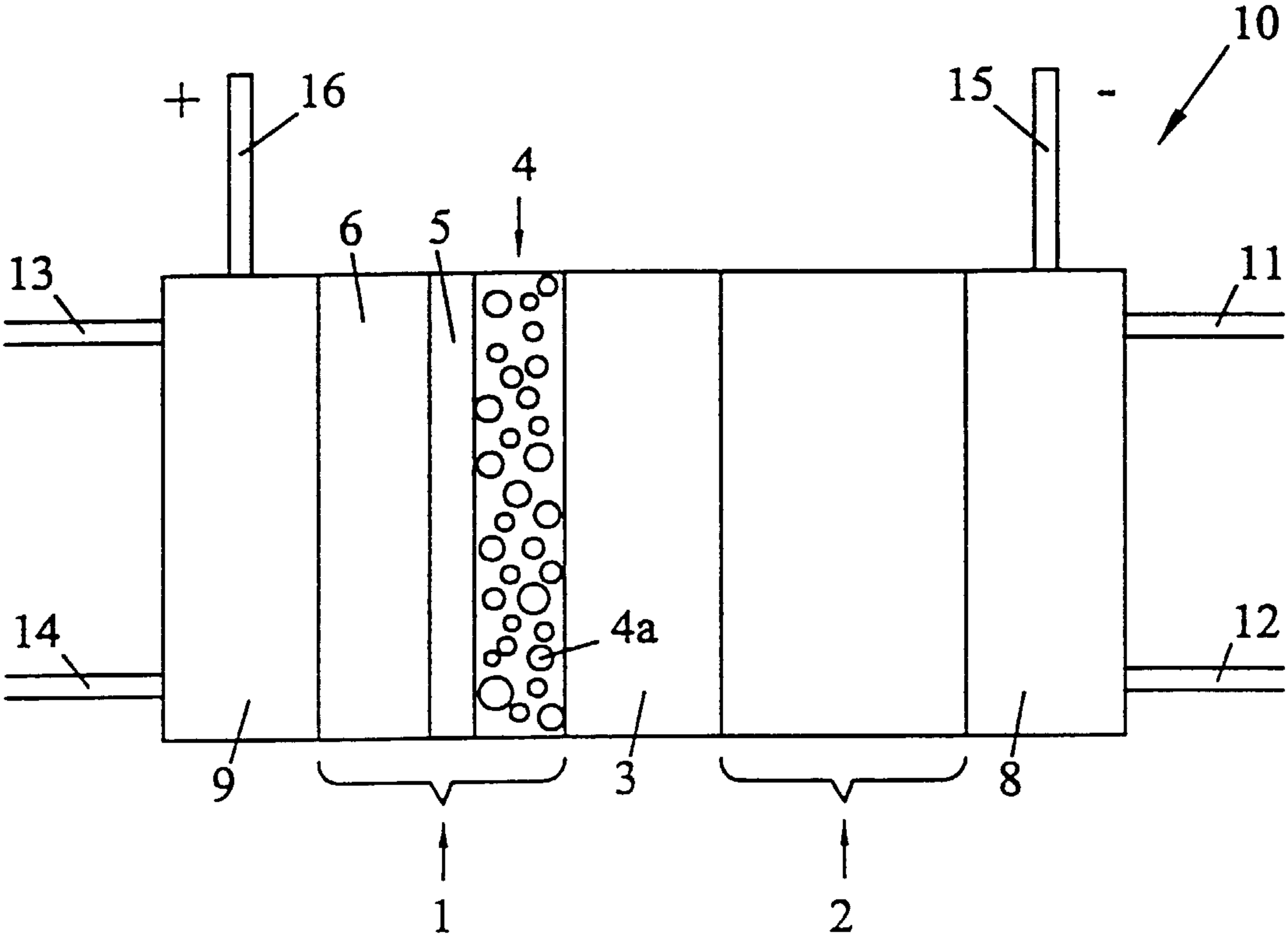

0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
Cell voltage (V)
L
K
J
1.0
1.5
2.0
2.5
3.0
Oxidant stoichiometry

FIG. 4b


10
+
16
15
-
4
6
5
13
11
4a
14
12
9
3
8
1
2