Aug. 16, 1966 E. H. LYONS, JR 3,266,937

ELECTROLYTIC CELL HAVING A ROTATING ELEMENT

Filed Nov. 4, 1963

Fig. 1

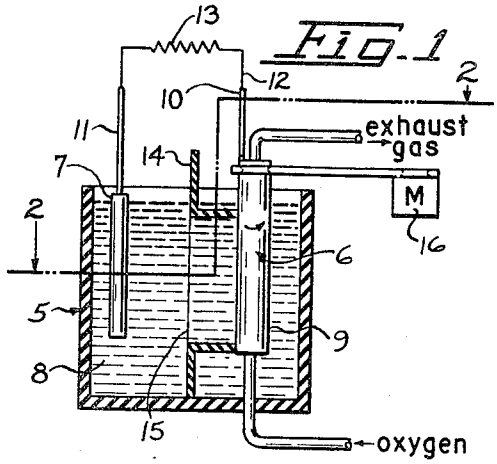


Fig. 2

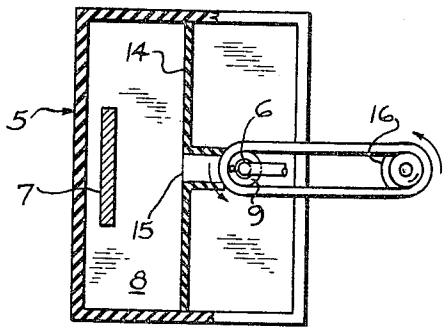


Fig. 3

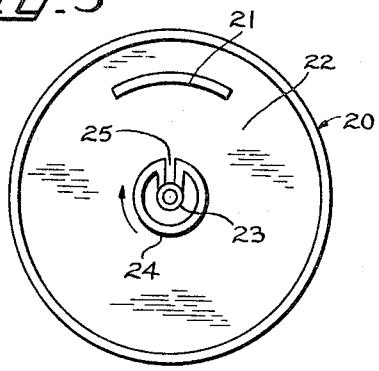
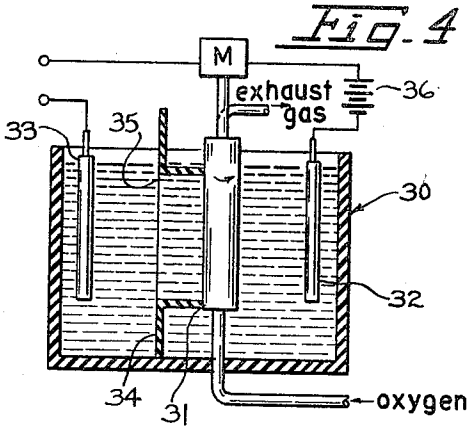


Fig. 4



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ELECTROLYTIC CELL HAVING A ROTATING ELEMENT

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16 Claims. (Cl. 136—86)

This application is a continuation-in-part of application Serial No. 186,665, filed April 11, 1962, now abandoned.

This invention relates to improvements in electrolytic cells of the type having an oxygen cathode, including the so-called air-depolarized primary voltaic cells and both direct and indirect fuel cells.

Such cells supply electric current to an external circuit as a result of electrochemical reactions within the cell. These reactions are not yet fully understood, but a net result is an oxidation reaction at the anode where electrons are produced, and the electrons return through the exterior circuit to the cathode, where oxygen is supplied to the electrolyte in order to sustain the oxidation reaction at the anode. The oxygen cathode comprises a catalytic metal member or a porous carbon member impregnated with catalytic oxides against or through which a stream of oxygen is passed into the electrolyte, usually a solution. Various electrolytes—acidic, basic, and neutral—are well known, and various anodes are used, including metals, hydrogen, metal compounds capable of oxidation and other reducing agents. The present invention is not especially concerned with the exact nature of the anode.

Whatever the anode and electrolyte, known thermodynamic data enable electrochemists to calculate the voltage which should be produced in a cell having an oxygen cathode. These voltages differ, depending on the material that is oxidized at the anode, and their theoretical values are precisely determinable.

However, when such cells have actually been built, the theoretical voltages have not generally been attained; in fact, the measured voltages have commonly been far below the theoretical values, not only when current is flowing, as the result of polarizations of various kinds, but also on open circuit. It has generally been supposed that the reduction of oxygen at these electrodes proceeds only to the peroxide state, because they have exhibited potentials less than the theoretical voltages expected from reduction of oxygen to water. Even though catalytic effects from specific electrode surfaces result in raising the voltage by decomposing the peroxide so rapidly that its concentration is minimal (sometimes estimated at 10^{-7} M.) and the oxygen so produced is re-reduced, so that it is ultimately consumed in a net four-electron reduction, the potential expected for reduction of oxygen to water has not heretofore been attained. This failure has represented a substantial loss in power output of the cell.

The reduction in voltage below the open-circuit value, sometimes referred to as "overvoltage," has been attributed to polarization of the cell. Three types of such polarization are recognized: (1) resistance polarization, due to the resistance of the solution which results in an IR drop, (2) activation polarization, connected with the finite rate of time at which the chemical and electrochemical reactions take place at the electrode, and (3) concentration polarization, due apparently to concentration changes at the electrodes. By choosing a suitable electrolyte and using the minimum practical spacing of electrodes, the overvoltage due to the resistance drop of the solution can be held to a low value. Concentration polarization is often not too serious as to the amount of overvoltage it causes. Activation polarization has, however, often been a serious factor in reducing the actual voltage to only a fraction of the theoretical voltage.

Recent studies have shown that the electrochemical reactions in the vicinity of an oxygen cathode are far more complex than had been believed heretofore, but these studies have not solved the problem of how to obtain actual voltage outputs approaching the theoretical values.

An important object of this invention is to enable one to get a substantially higher voltage from a cell with an oxygen electrode.

Other objects and advantages of the invention will become clear from the following description.

I have found that in the first few milliseconds of the reduction at certain catalytic surfaces, including platinum, palladium, nickel, cobalt, and iron oxides, the reduction proceeds to water. However, subsequently the oxides are removed or altered by electroreduction, and their ability to effect reduction to water is impaired or eliminated, and reduction to peroxide sets in, with consequent power loss; this may be termed deactivation of the catalyst.

Moreover, I have discovered that by cyclically employing different portions of the cathode activity while the other portions rest, deactivation of the catalyst can largely be avoided. Apparently, when the cell current is substantially stopped from flowing at a portion of the cathode, there is a tendency to restore the activity of the surface, particularly in alkaline electrolyte. Consequently, cycling the effective portion of the electrode maintains the desired type of active surface.

The time intervals involved in both deactivation and reactivation are quite short, and my invention uses them to obtain an increase in actual voltage by providing a rapid rotation, usually at a speed of several revolutions per second, of the cathode or of a shield associated with it. The voltage obtained is fairly steady and much higher than can be obtained from a conventional cathode. Banks of cells can be used to produce practically any desired current and voltage.

In some instances the restoration of activity to the cathode surface, presumably through chemical oxidation by oxygen dissolved in the electrolyte or supplied in some other way, is inconveniently slow. I have found that the restoration may be hastened by providing intimate contact with a metal surface which is less active (more cathodic) than the oxide surface to be activated. Thus, a partial coating of palladium on platinum greatly increases the reactivation. Other combinations are platinum-nickel, platinum - silver, platinum - gold, nickel - silver, nickel-gold, etc. The use of copper, silver, or gold as the activating addend is particularly effective since these metals do not as readily form oxide layers of their own. The addend metals may be applied by electrodeposition, flame-spraying, powder metal techniques, or in other suitable ways. Alternatively, reactivation of the cathode catalyst can be speeded by supplying an anodic potential during a portion of the resting period by means of an auxiliary cathode, as described more fully later.

The invention will be easier to understand by considering the following drawings, in which:

FIG. 1 is a somewhat diagrammatic view of an electrolytic cell embodying the principles of the invention, the cell being shown generally in elevation and in section.

FIG. 2 is a generally top plan schematic view of the cell of FIG. 1.

FIG. 3 is a top plan view, generally diagrammatic, of a modified cell also embodying the principles of the invention.

FIG. 4 is a view in elevation of still another modified form of cell embodying the principles of the present invention.

The principles of the invention may be illustrated by considering several specific examples. Thus, FIGS. 1 and

2 diagrammatically illustrate a cell **5** having an oxygen cathode **6**, an anode **7**, and an electrolyte **8**. The cathode **6** may comprise a tube **9** of graphite, or porous platinum or a fine screen of platinum. Nickel, nickel oxide, and silver are other suitable conductive materials, and of course many other materials are also suitable at the cathode **6**. The purpose is to get oxygen into the solution **8**. Oxygen may be supplied to the hollow interior of the tube **9** and pass to the active surface by means of openings or pores, or oxygen may be bubbled through a sparger located below the cathode **6** and reach the exterior surface of the cathode **6** by physical contact of the rising gas bubbles, or by diffusion, as gas dissolved in the electrolyte. The anode **7** may be a lower metallic oxide (e.g., Cu_2O, CoO, PbO, Mn_3O_4, Fe_3O_4) as disclosed in my co-pending application, Serial No. 840,196, filed September 15, 1959, now Patent No. 3,100,163, or the anode may be hydrogen or other oxidizable material. The electrolyte **8** for this cell **5** is preferably basic (e.g., 20% KOH or NaOH in water) because the base helps to maintain or restore the active surface of the cathode. The cathode **6** has a terminal **10**, and the anode **7** has a terminal **11**, which are connected together by a lead **12** through a load **13**.

For example, in a copper oxide-oxygen cell using potassium hydroxide as electrolyte, the theoretical voltage is about 0.56 volt, but when using the cell as so far described, there is an overvoltage of 0.25 to 0.30 volt, cutting the actual voltage to about half of the theoretical value.

My invention incorporates a shield **14** confining direct communication between the anode **7** and cathode **6** to a narrow area defined as a slit **15** in the shield **14**. The shield **14** is preferably of an insulating material that is not attacked by the electrolyte and may be provided with flanges **14***a* or whatever is necessary to confine the direct communications to passage through the slit **15**. In the form of the invention shown in FIGS. 1 and 2, I also provide suitable means **16** (such as a constant speed motor) for rotating the cathode **6**, preferably at a speed greater than 2 revolutions per second. As a result, only a small portion of the surface of the cathode **6** is actually in use at any one time, and the remainder is being depolarized and reactivated while resting.

The open-circuit voltage of such a cell indicates that the reduction occurring is oxygen to water, being much higher than what would obtain if there were reduction to peroxide. When the cathode **6** is rotated too slowly, the potential drops toward that expected for reduction to peroxide, whereas proper rotation at the correct speeds results in partial recovery of the initial voltage; hence reduction to water retains its predominance.

The surface state of the electrode is extremely important, as previously indicated. Some electrodes recover their activity for reduction to water very much more rapidly than others, the time for complete recovery varying from 30 seconds to 45 minutes, after polarization and deactivation had proceeded to a substantially steady value. Two types of voltage-shift are observed with stationary electrodes, and it is presumed that they tend to occur also with rotating electrodes, but since current is produced by the areas next to the slit, effects which accompany longer periods of electrode activity are actually observed only at relatively slow speeds of rotation. One of these types of voltage shift is quite rapid under load, and is followed by a rapid recovery, or at least a partial recovery when the current flow is interrupted. This shift is due to the usual causes of polarization. It can be minimized by appropriate arrangement of the oxygen supply and agitation of the electrolyte. The other is due to a more gradual change in the electrode reaction, from one of reduction to water to another of reduction to peroxide. This second change is slower and more profound, and appears to be the result of a change in the condiiton of the oxide film on the electrode. It is not polarization in the usual electrochemical sense, although it satisfies the formal definition of polarization.

The advantages of the present invention are partly due to diminished concentration polarization, because diffusion operates during idle periods as well as during the action periods of each surface portion to dissipate the concentration gradients. However, the greater part of the advantage of the rest periods resulting from rotation is the maintenance of a more active electrode surface, as indicated by effective potentials. It is supposed that this is connected with the type or condition of the oxide film. The importance of this surface condition is quite great.

The cell **20** shown in FIG. 3 has an anode **21**, an electrolyte **22**, and a cathode **23** surrounded by a shield **24** having a generally vertical slit **25**. In this form of the invention, the cathode **23** remains stationary and the shield **24** rotates, so that the slit **25** successively exposes the surface of the cathode **23** to the electrolytic action. The effect is in many ways the same as before with the differences that the change implies. When the slit **25** is on the side of the cathode **23** away from the anode **21**, there is a longer path of current flow than when it is exposed directly to the anode. The increase in resistance resulting from this circumstance is, in the concentric cylindrical arrangement shown in the sketch, not great, but it can be made negligible by providing a series of anodes **21** arranged circumferentially around the cathode or by making the anode **21** itself cylindrical, surrounding and concentric with the cathode **23** and shield **24**.

In certain conditions, as with acid electrolytes, it is advantageous to impress a momentary anodic potential on the portions of the cathode at which depolarization and reactivation are taking place during resting periods, in order to accelerate, initiate, or extend the processes of recovery. Such a potential may be applied as shown in FIG. 4, in a cell **30** having a rotating catalytic electrode **31**, by means of an auxiliary cathode **32**, constructed of platium, nickel, graphite, or other suitable material, and placed next to the cathode **31** on the side away from the anode **33** and away from the slit **35** in the shield **34**. The auxiliary cathode **32** is connected externally to the primary cathode **31** through a battery **36** or other potential source, so that the primary cathode **31** is made anodic relative to the auxiliary cathode **32**; this does not disturb the cathodic functioning of the action area of the cathode **31** presented to the slit **35**. Although a small current flows directly between the auxiliary cathode **32** and the primary anode **33**, the electrical resistance of this path is very much greater than that of the path between the auxiliary cathode **32** and the primary cathode **31**; furthermore, the arrangement of the primary cathode **31**, the shield **34**, and its slit **35** tends to screen the auxiliary cathode **32** from the primary anode **33**; in consequence, this "leakage" current is negligible. Presumably the electrode reaction at the auxiliary cathode **32** is reduction of oxygen to peroxide, since no provision is made for maintaining activity with respect to reduction to water. The potential applied between the two cathodes **31** and **32** is adjusted so that the resulting current is a small fraction (0.1–10%) of that flowing between the primary electrodes **31** and **33**, and being withdrawn through terminals **11** and **12**.

To those skilled in the art to which this invention relates, many changes in construction and widely differing embodiments and applications of the invention will suggest themselves without departing from the spirit and scope of the invention. The disclosures and the description herein are purely illustrative and are not intended to be in any sense limiting.

I claim:

1. Electrical apparatus of the type having a cell with an anode, an electrolyte, and an oxygen cathode having means for supplying gaseous oxygen to the cell at a catalytic surface of a solid cathode member, so that an oxidation reaction takes place at the anode, thereby caus-

ing current to flow externally through a load circuit connecting the anode and cathode,

characterized by

means for cyclically using successive catalytic surface portions of said solid cathode member in the passage of current within said cell from said cathode to said anode, the catalytic surface portion not currently being used remaining continuously immersed in said electrolyte and thereby having rest periods while in said electrolyte, at a rate rapid enough to maintain the cell in an active state in respect to the electro-reduction of oxygen to water.

2. Electrical apparatus of the type having a cell with an anode, an electrolyte, and an oxygen cathode including means for supplying gaseous oxygen to the cell at a catalytic surface of a solid cathode member, so that an oxidation reaction takes place at the anode, thereby causing current to flow externally through a load circuit connecting the anode and cathode and wherein deactivation of the catalyst tends to reduce the cell voltage a substantial amount below the theoretical voltage obtainable,

characterized by

means for cyclically using successive catalytic surface portions of said solid cathode member in the passage of current within said cell from said cathode to said anode, at a rate rapid enough to pass current at a relatively activated catalyst state, the surface portion not currently being used remaining continuously immersed in said electrolyte and thereby having rest periods while in said electrolyte adequate to maintain the catalyst in a substantially activated condition.

3. Electrical apparatus of the type having a cell with an anode, an electrolyte, and an oxygen cathode means for supplying gaseous oxygen to the cell at a catalytic surface of a solid cathode member so that an oxidation reaction takes place at the anode, thereby causing current to flow externally through a load circuit connecting the anode and cathode,

characterized by

shield means at said cathode between said anode and said solid cathode member having a slit limiting ionic communication between said anode and said solid cathode member to a relatively small exposed electrolytic surface area of said solid cathode member, and

means for rotating said cathode at a frequency rapid enough to maintain the cell in active state in respect to the electro-reduction of oxygen to water.

4. Electrical apparatus of the type having a cell with an anode, an electrolyte, and an oxygen cathode means for supplying gaseous oxygen to the cell at a catalytic surface of a solid cathode member so that an oxidation reaction takes place at the anode, thereby causing current to flow externally through a load circuit connecting the anode and cathode and wherein deactivation of the catalyst tends to reduce the cell voltage a substantial amount below the theoretical voltage obtainable,

characterized by

shield means at said cathode between said anode and said solid cathode member having a slit exposing a portion of said cathode member for enabling ionic communication between said anode and said solid cathode member while preventing passage of current to other portions of said cathode member and

means for rotating said cathode at a frequency rapid enough to pass current at a relatively activated cell state.

5. Electrical apparatus of the type having a cell with an anode, an electrolyte, and an oxygen cathode means for supplying gaseous oxygen to the cell at a catalytic surface of a solid cathode member so that an oxidation

reaction takes place at the anode, thereby causing current to flow externally through a load circuit connecting the anode and cathode,

characterized by

shield means at said cathode between said anode and said solid cathode member having a slit therethrough for confining ionic communication between said anode and cathode substantially to the slit area, and

means for rotating said shield means around said cathode at a frequency rapid enough to maintain said cell in active state in respect to the electro-reduction of oxygen to water.

6. Electrical apparatus of the type having a cell with an anode, an electrolyte, and an oxygen cathode means for supplying gaseous oxygen to the cell at a catalytic surface of a solid cathode member so that an oxidation reaction takes place at the anode, thereby causing current to flow externally through a load circuit connecting the anode and cathode and wherein deactivation of the catalyst tends to reduce the cell voltage a substantial amount below the theoretical voltage obtainable,

characterized by

shield means at said cathode interposed between said anode and said solid cathode member having a slit therethrough defining the ionic communication path between said anode and cathode to a limited area of the cathode, and

means for rotating said shield means around said cathode at a frequency rapid enough to pass current at a relatively activated catalyst state.

7. Electrical apparatus of the type having a cell with an anode, an electrolyte, and an oxygen cathode means for supplying gaseous oxygen to the cell at a catalytic surface of a solid cathode member so that an oxidation reaction takes place at the anode, thereby causing current to flow externally through a load circuit connecting the anode and cathode,

characterized by

a shield between said cathode member and said anode, having a window therethrough closely adjacent said cathode and limiting ionic communication to said cathode to the area exposed by said window, and

means for rotating said cathode at a frequency of at least 2 times per second.

8. Electrical apparatus of the type having a cell with an anode, an electrolyte, and an oxygen cathode means for supplying gaseous oxygen to the cell at a catalytic surface of a solid cathode member so that an oxidation reaction takes place at the anode, thereby causing current to flow externally through a load circuit connecting the anode and cathode,

characterized by

a shield surrounding said cathode member and having a window therethrough closely adjacent said cathode to limit ionic communication to the cathode area immediately at said window, and

means for rotating said shield at a frequency of at least 2 times per second.

9. Electrical apparatus of the type having a cell with an anode, an electrolyte, and an oxygen cathode means for supplying gaseous oxygen to the cell at a catalytic surface of a solid cathode member so that an oxidation reaction takes place at the anode, thereby causing current to flow externally through a load circuit connecting the anode and cathode and wherein deactivation of the catalyst tends to reduce the cell voltage a substantial amount below the theoretical voltage obtainable,

characterized by

a shield at said cathode between said cathode member and said anode, having a window therethrough, so that ionic communication between the anode and the cathode lies only through

said window to only the cathode portion exposed by said window,

a secondary cathode on the opposite side of said shield from said anode,

means for maintaining said secondary cathode cathodic with respect to said cathode member so as to anodize the side of said cathode member closest to said secondary cathode, and

means for rotating said cathode at a frequency of at least 2 times per second, thereby maintaining the activity of said catalytic surface.

10. A method of maximizing the voltage of an electrolytic cell of the type having an anode, an electrolyte, and an oxygen cathode means for supplying gaseous oxygen to the cell at a catalytic surface of a solid cathode member so that an oxidation reaction takes place at the anode, thereby causing current to flow externally through a load circuit connecting the anode and cathode,

characterized by

cyclically using successive surface portions of said catalytic surface of said solid cathode member in the passage of current within said cell from said cathode to said anode, the catalytic surface portion not currently being used being continuously retained immersed in said electrolyte and thereby having rest periods while in said electrolyte, at a rate rapid enough to maintain the cell in an active state in respect to the electro-reduction of oxygen to water.

11. A method of preventing to some extent polarization and deactivation of an electrolytic cell of the type having an anode, an electrolyte, and an oxygen cathode means for supplying gaseous oxygen to the cell at a catalytic surface of a solid cathode member so that an oxidation reaction takes place at the anode, thereby causing current to flow externally through a load circuit connecting the anode and cathode and wherein deactivation of the catalyst tends to reduce the cell voltage a substantial amount below the theoretical voltage obtainable,

characterized by

cyclically using successive surface portions of said catalytic surface of said solid cathode member in the passage of current within said cell from said cathode to said anode, at a rate rapid enough to pass current at a relatively unpolarized cell state and at a relatively activated catalyst state, the catalytic surface portion not currently being used being continuously in contact with and immersed in said electrolyte thereby having rest periods in said electrolyte adequate to maintain the cell in a substantially activated condition.

12. A method of operating an electrolytic cell of the type having an anode, an electrolyte, and an oxygen cathode means for supplying gaseous oxygen to the cell at a catalytic surface of a solid cathode member so that an oxidation reaction takes place at the anode, thereby causing current to flow externally through a load circuit connecting the anode and cathode,

characterized by

preventing passage of current between said anode and said solid cathode member except at a small fraction of the surface of the solid cathode member, and

rotating said cathode entirely immersed within said electrolyte at a frequency rapid enough to maintain the catalytic surface in active state in respect to the electro-reduction of oxygen to water.

13. A method of maintaining in a relatively unpolarized and activated state an electrolytic cell of the type having an anode, an electrolyte, and an oxygen cathode with means for supplying gaseous oxygen to the cell at a catalytic surface of a solid cathode member so that an oxidation reaction takes place at the anode, thereby causing current to flow externally through a load circuit connecting the anode and cathode and wherein polarization of the cell and deactivation of the catalyst tends to reduce the cell voltage a substantial amount below the theoretical voltage obtainable,

characterized by

shielding said solid cathode member, except for a narrow passageway for current at said catalytic surface, between said anode and said solid cathode member, and

rotating said cathode at a frequency rapid enough to maintain activation of the catalytic surface exposed to said narrow passageway while keeping said cathode immersed at all times in said electrolyte.

14. A method of operating an electrolytic cell of the type having an anode, an electrolyte, and an oxygen cathode means for supplying gaseous oxygen to the cell at a catalytic surface of a solid cathode member so that an oxidation reaction takes place at the anode, thereby causing current to flow externally through a load circuit connecting the anode and cathode, said solid cathode member being fully immersed at all times in said electrolyte,

characterized by

enclosing said solid cathode member except for a narrow slit parallel to the axis of the cathode member and

rotating said slit relative to said cathode at a frequency rapid enough to maintain said catalytic surface at said slit in active state in respect to the electro-reduction of oxygen to water.

15. A method of operating an electrolytic cell of the type having an anode, an electrolyte, and an oxygen cathode means for supplying gaseous oxygen to the cell at a solid cathode member so that an oxidation reaction takes place at the anode, thereby causing current to flow externally through a load circuit connecting the anode and cathode, said solid cathode member being fully immersed at all times in said electrolyte,

characterized by

shielding said cathode member from said anode, except for a small axial zone, and

rotating said cathode relative to said shield at a frequency of at least 2 times per second.

16. A method of operating an electrolytic cell of the type having an anode, an electrolyte, and an oxygen cathode means for supplying gaseous oxygen to the cell at a catalytic surface of a solid cathode member so that an oxidation reaction takes place at the anode, thereby causing current to flow externally through a load circuit connecting the anode and cathode and wherein deactivation of the catalyst tends to reduce the cell voltage a substantial amount below the theoretical voltage obtainable,

characterized by

allowing ionic communication between said cathode member and said anode at only a narrow passage along the plane joining them,

maintaining said cathode member fully immersed in said electrolyte at all times during operation,

rotating said cathode at a frequency of at least 2 times per second, and

anodizing the portion of said cathode substantially unexposed to said passage,

thereby maintaining the catalyst exposed to said passage in a substantially activated state.

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