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(54) **METHODS FOR ELECTROCHEMICAL DEPOSITION OF MULTI-COMPONENT SOLDER USING CATION PERMEABLE BARRIER**

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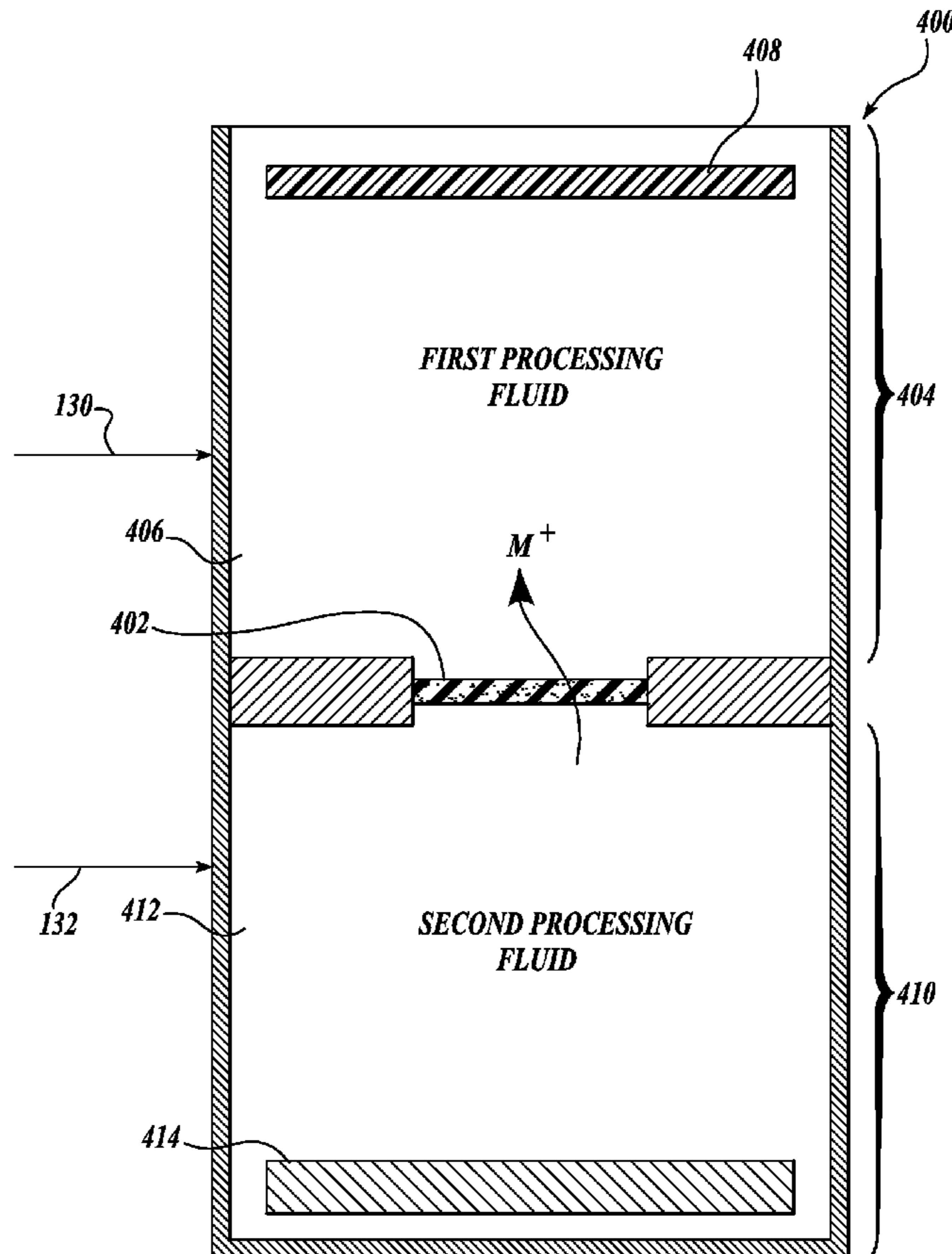
plication No. 11/414,145, filed on Apr. 28, 2006, now Pat. No. 8,236,159, which is a continuation-in-part of application No. 10/861,899, filed on Jun. 3, 2004, now Pat. No. 7,585,398, which is a continuation-in-part of application No. 10/729,357, filed on Dec. 5, 2003, now Pat. No. 7,351,315, which is a continuation-in-part of application No. 10/729,349, filed on Dec. 5, 2003, now Pat. No. 7,351,314.

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(57) **ABSTRACT**

Processes and systems for electrochemical deposition of a multi-component solder by processing a microfeature workpiece with a first processing fluid and an anode are described. Microfeature workpieces are electrolytically processed using a first processing fluid, an anode, a second processing fluid, and a cation permeable barrier layer. The cation permeable barrier layer separates the first processing fluid from the second processing fluid while allowing certain cationic species to transfer between the two fluids.



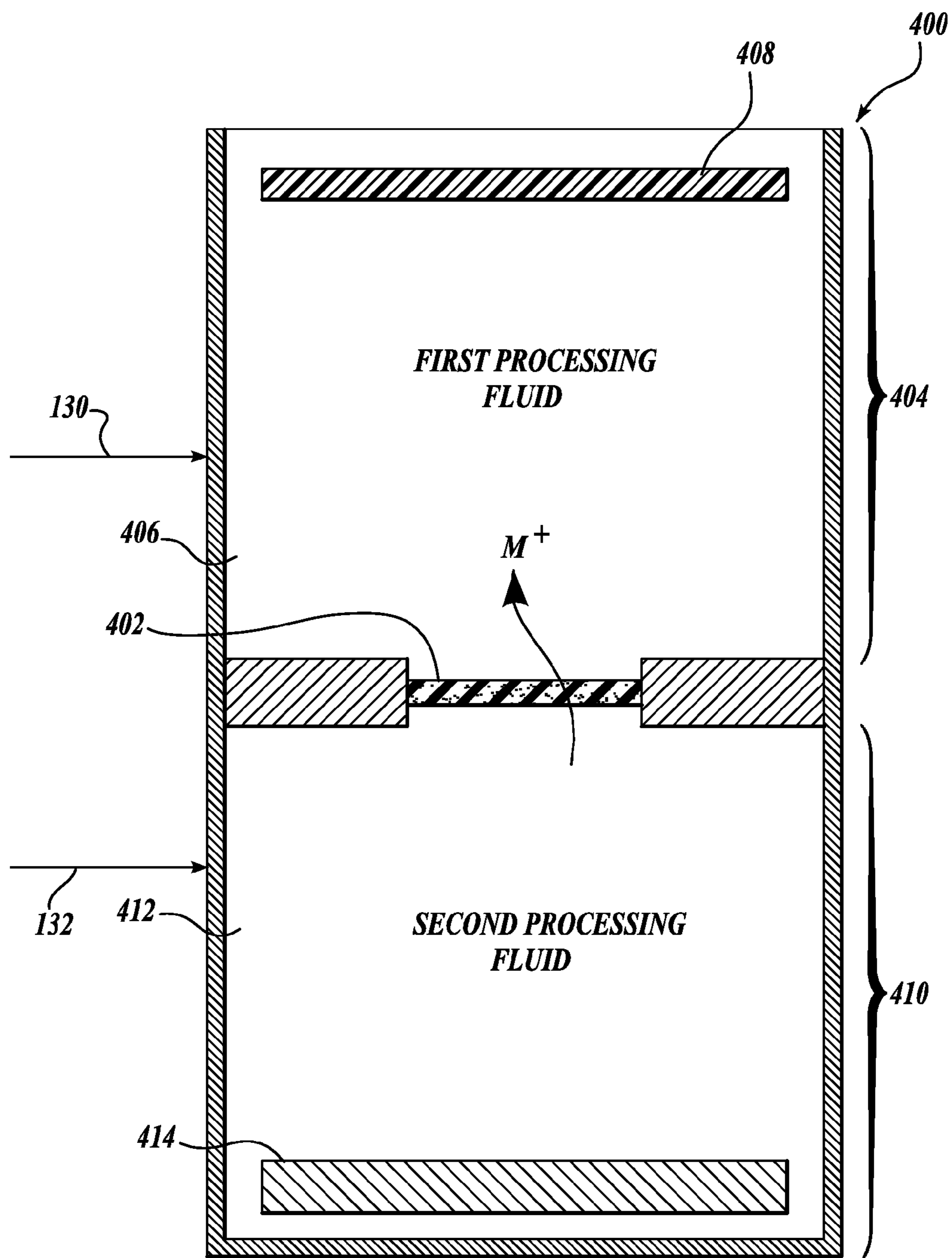


Fig. 1.

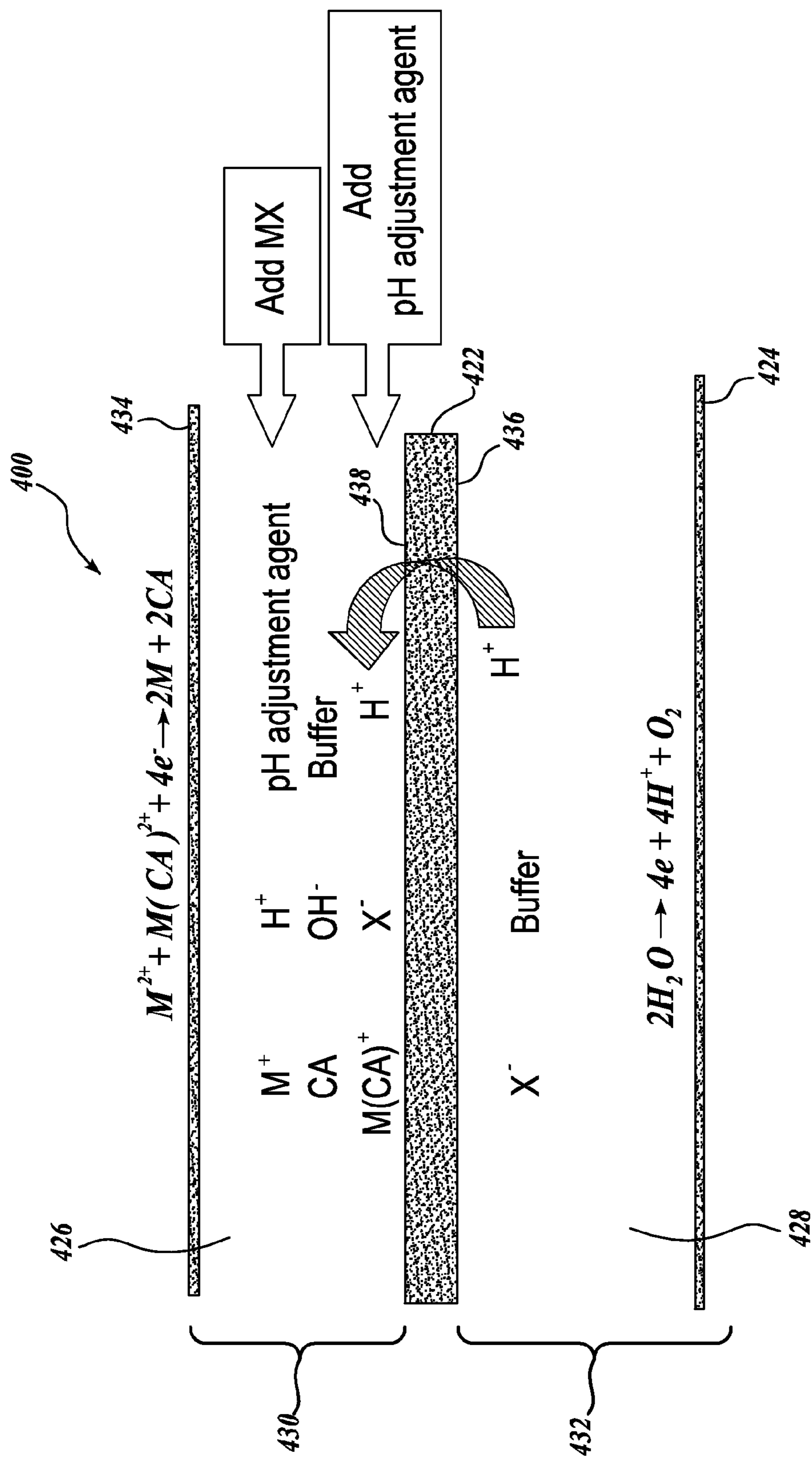


Fig. 2.

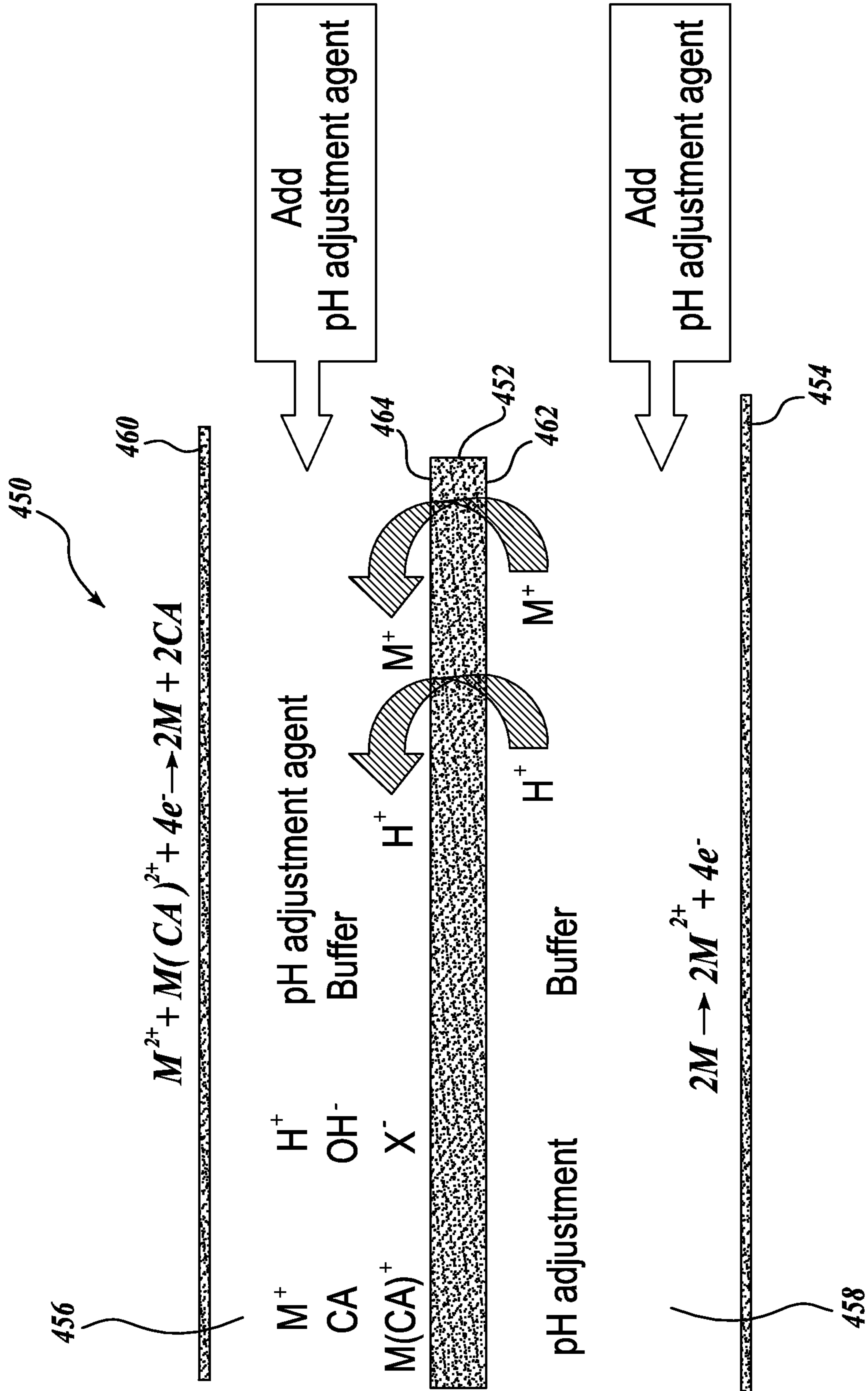


Fig. 3.

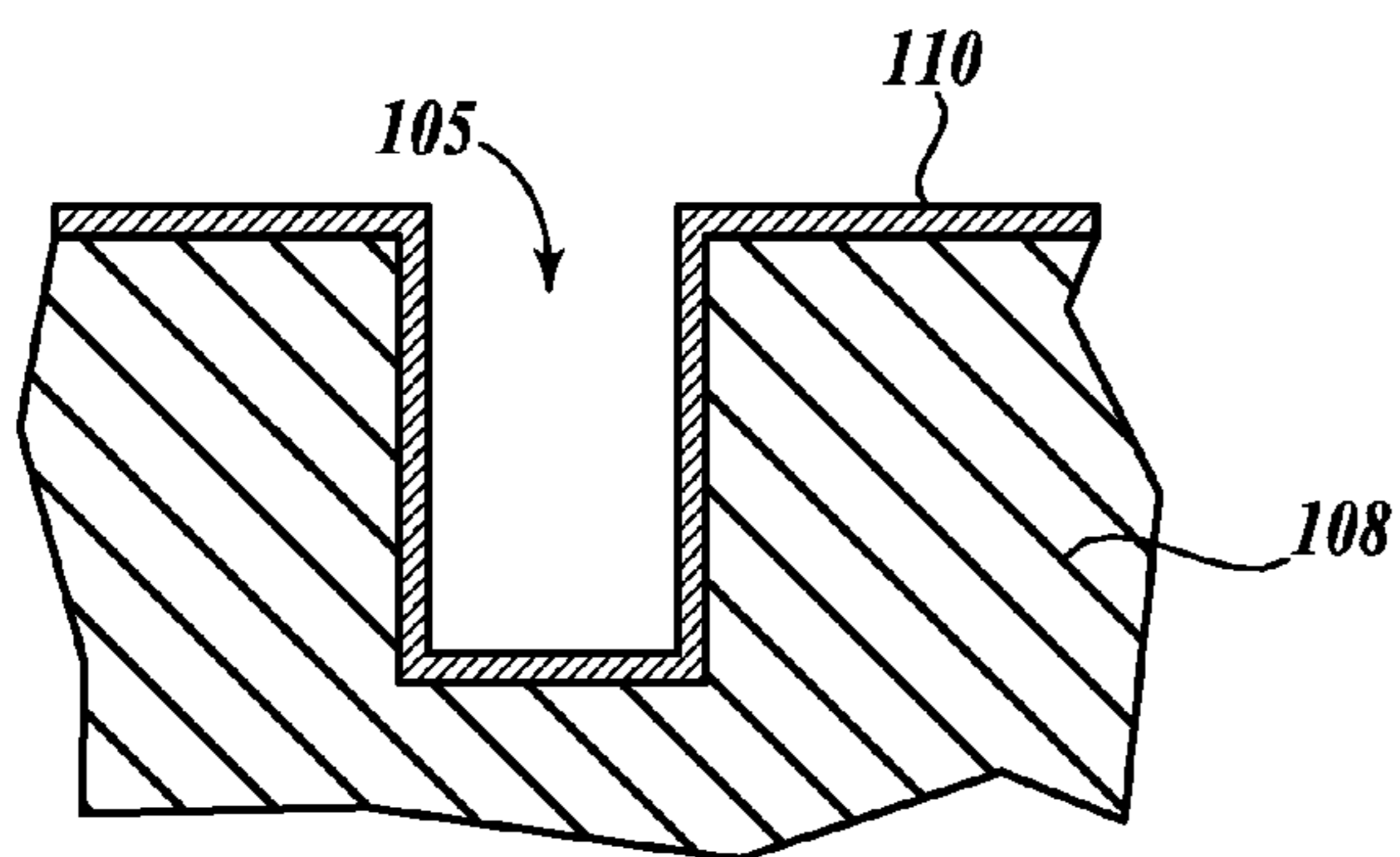


Fig. 4A.

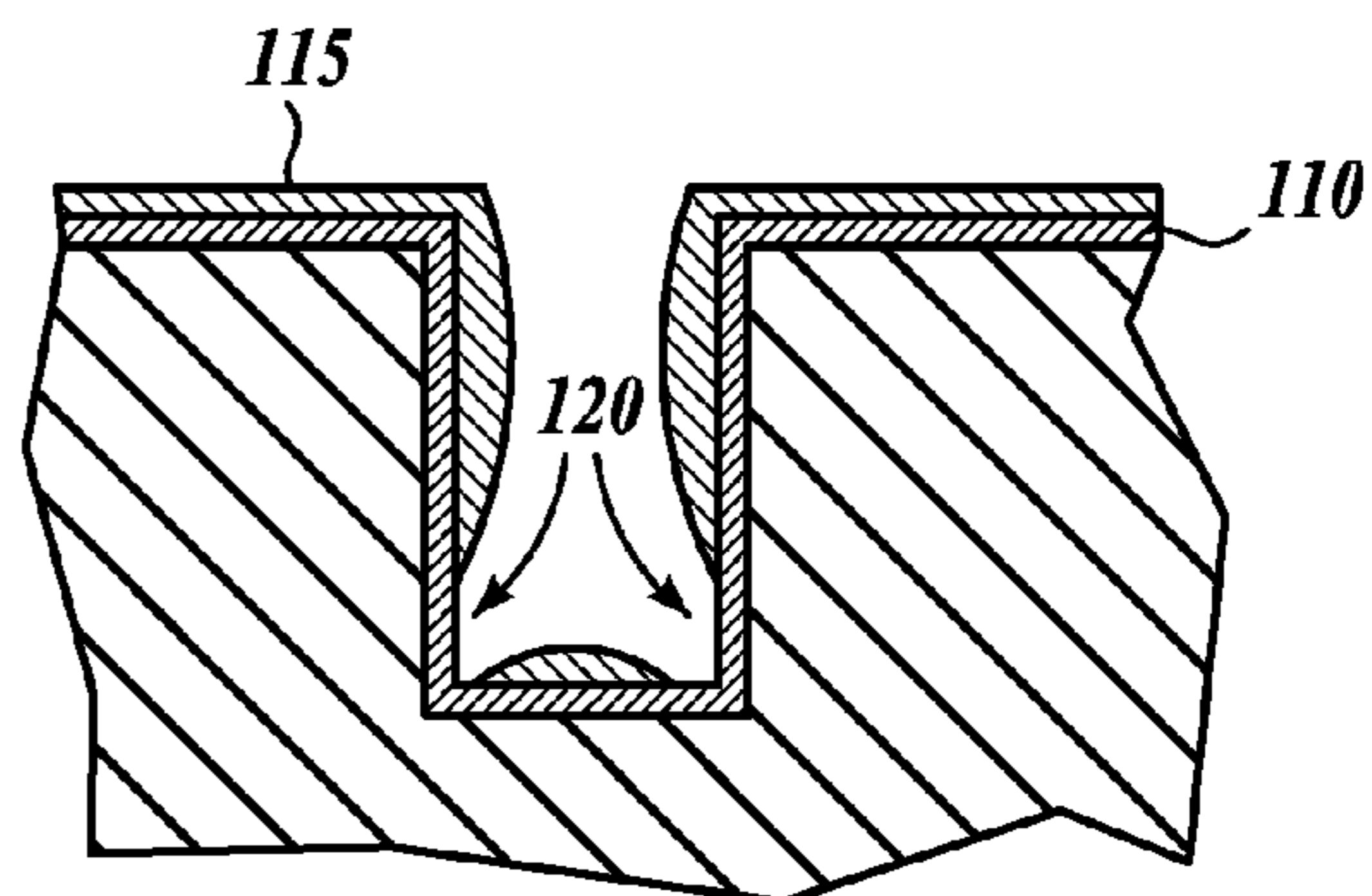


Fig. 4B.

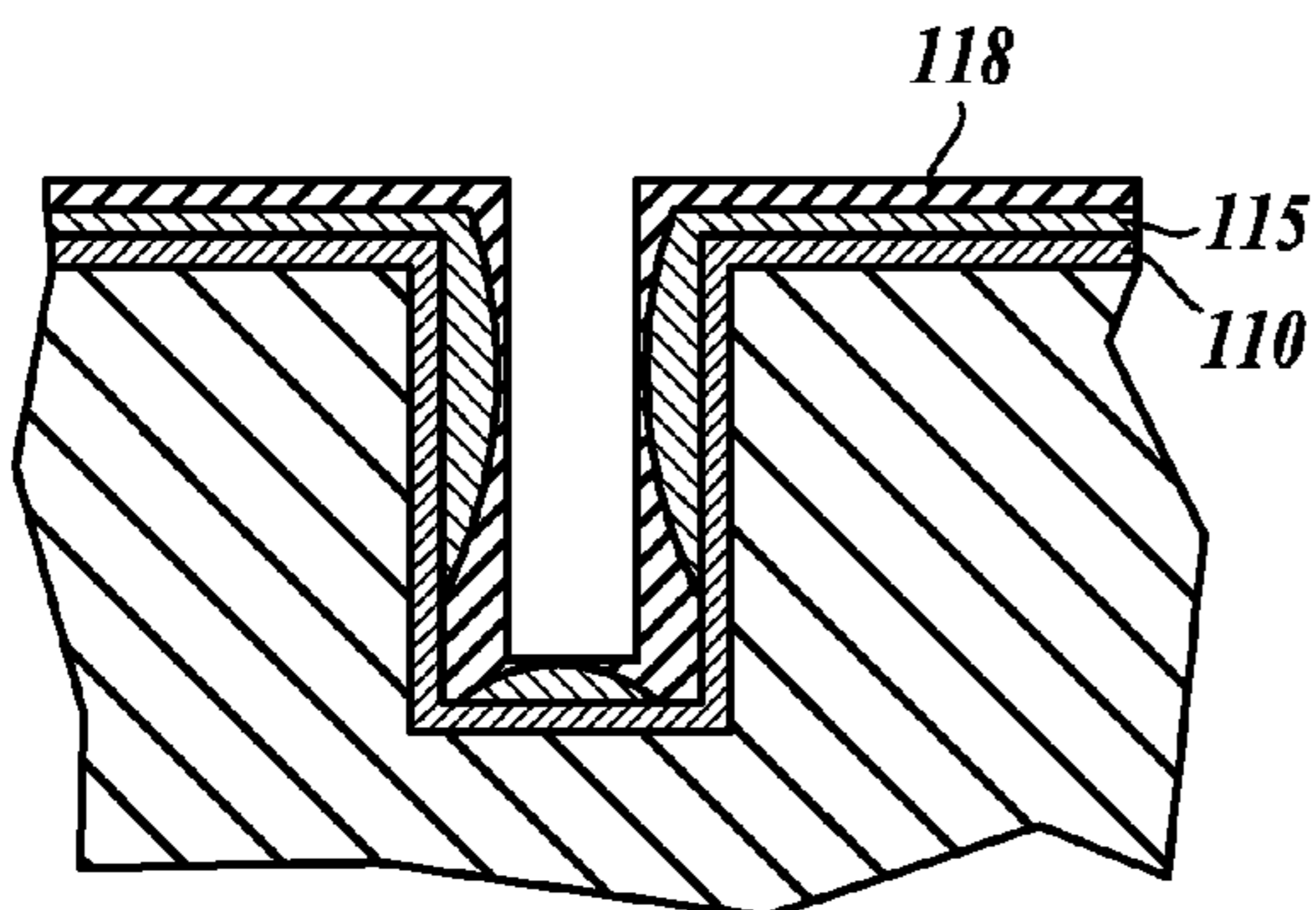


Fig. 4C.

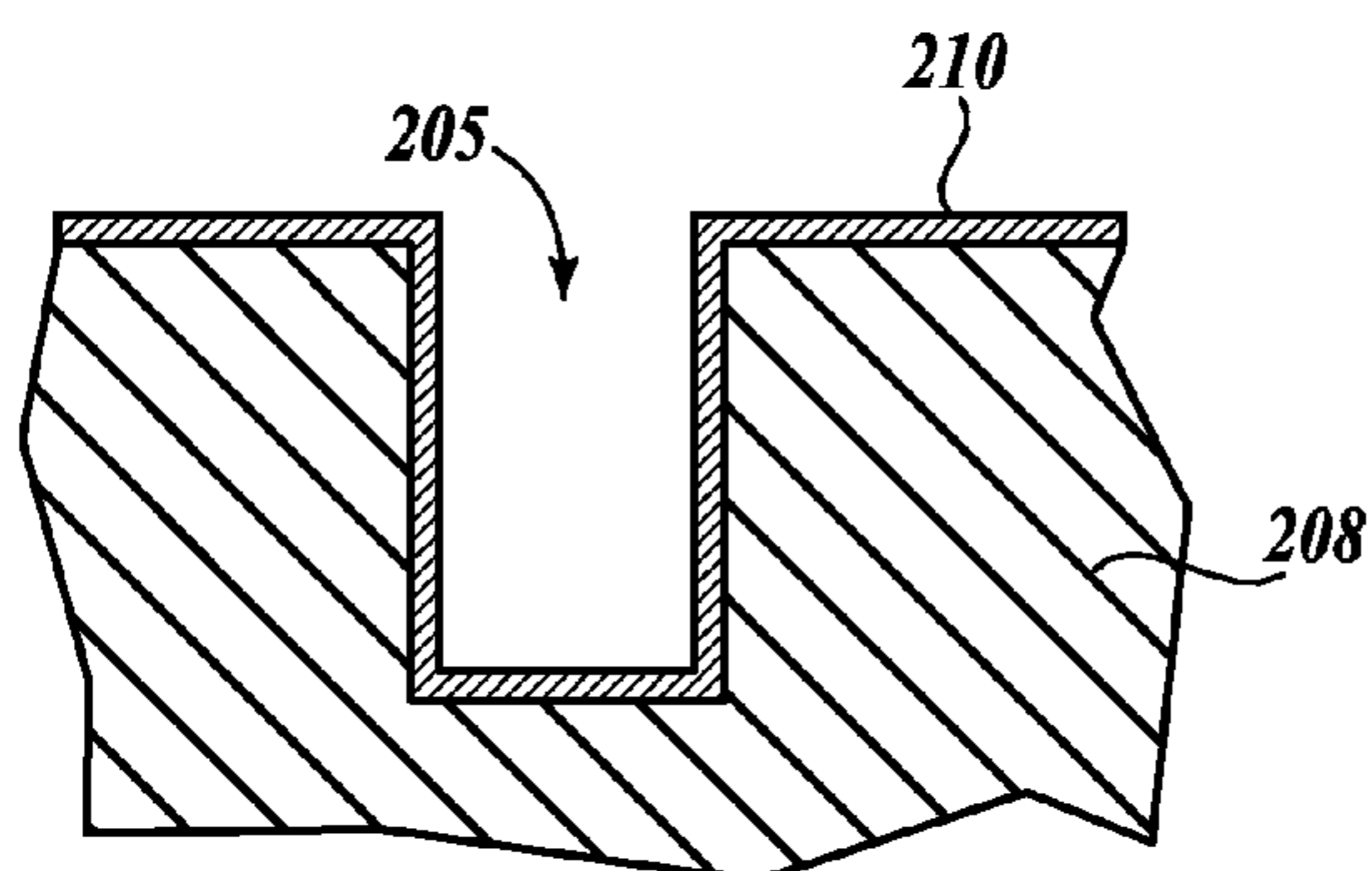


Fig. 5A.

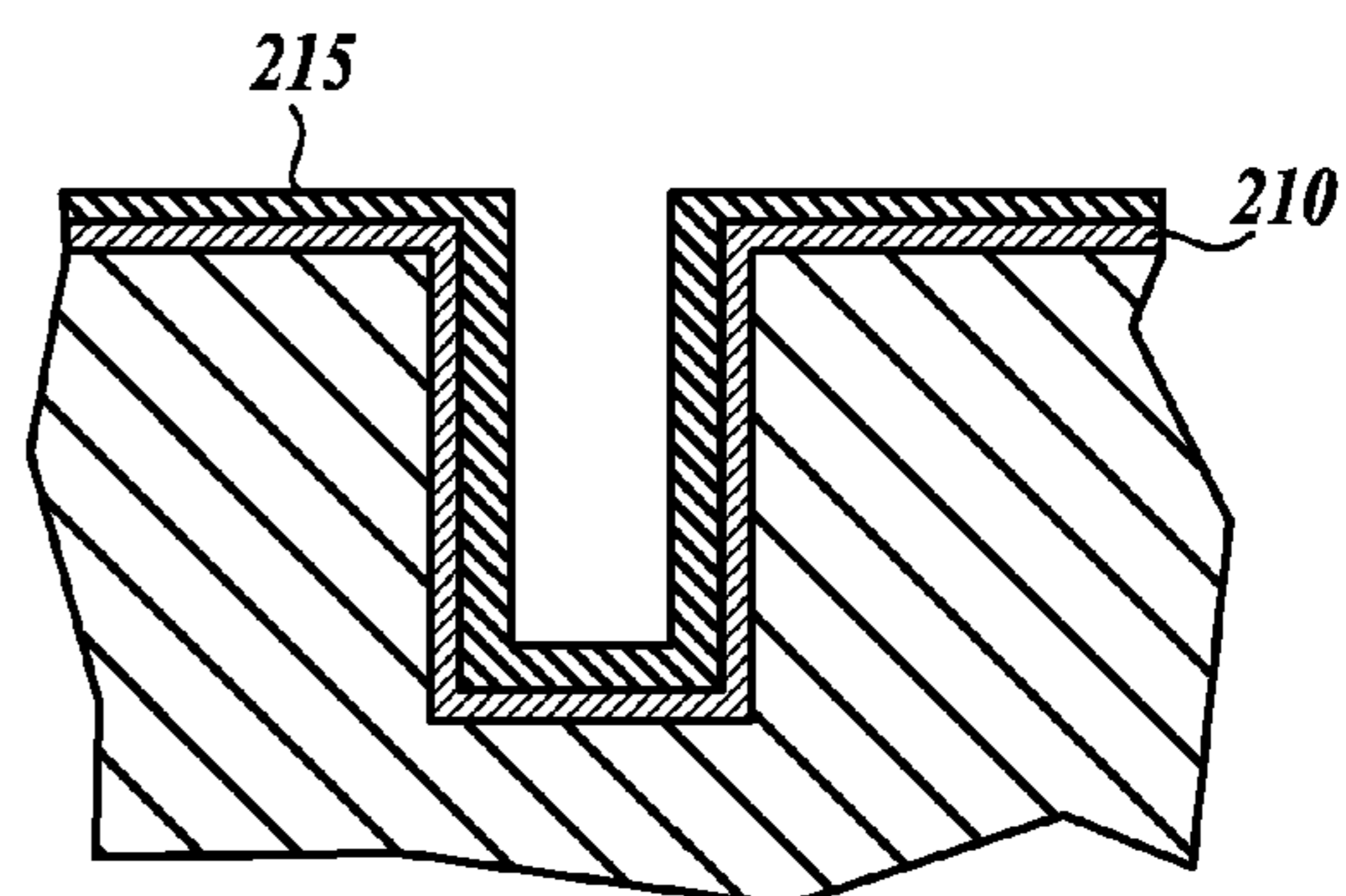


Fig. 5B.

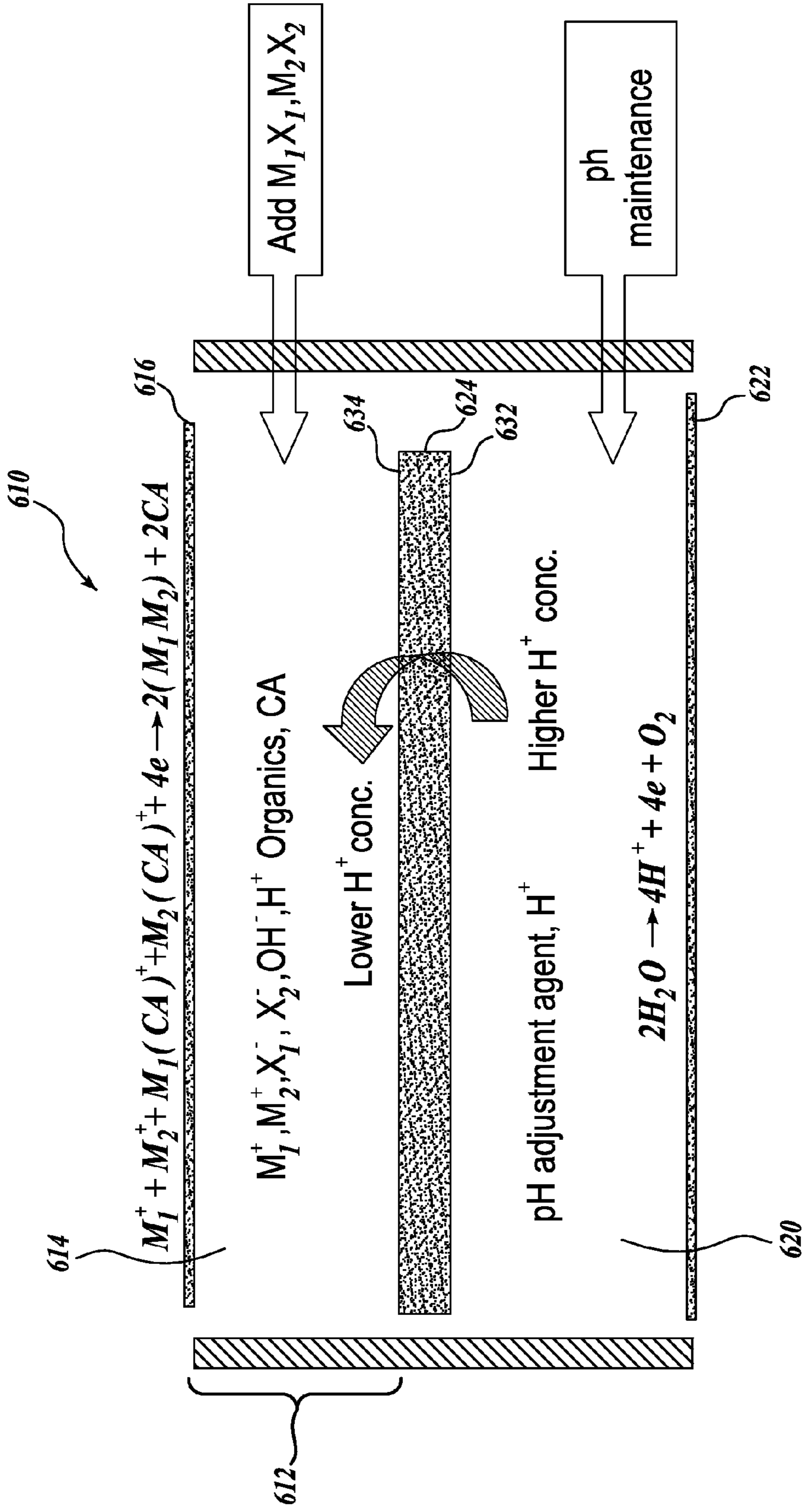


Fig. 6.

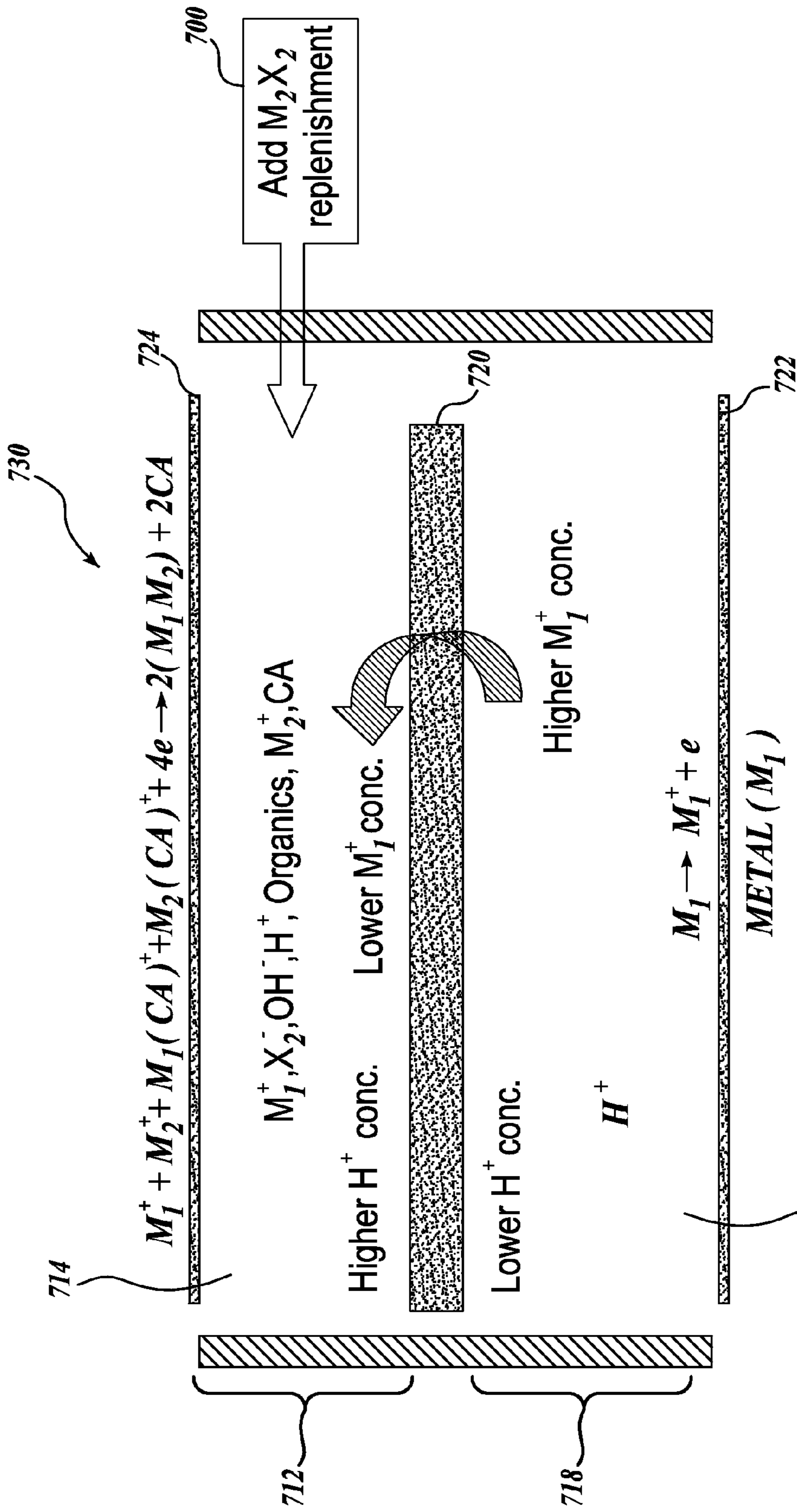


Fig. 7.

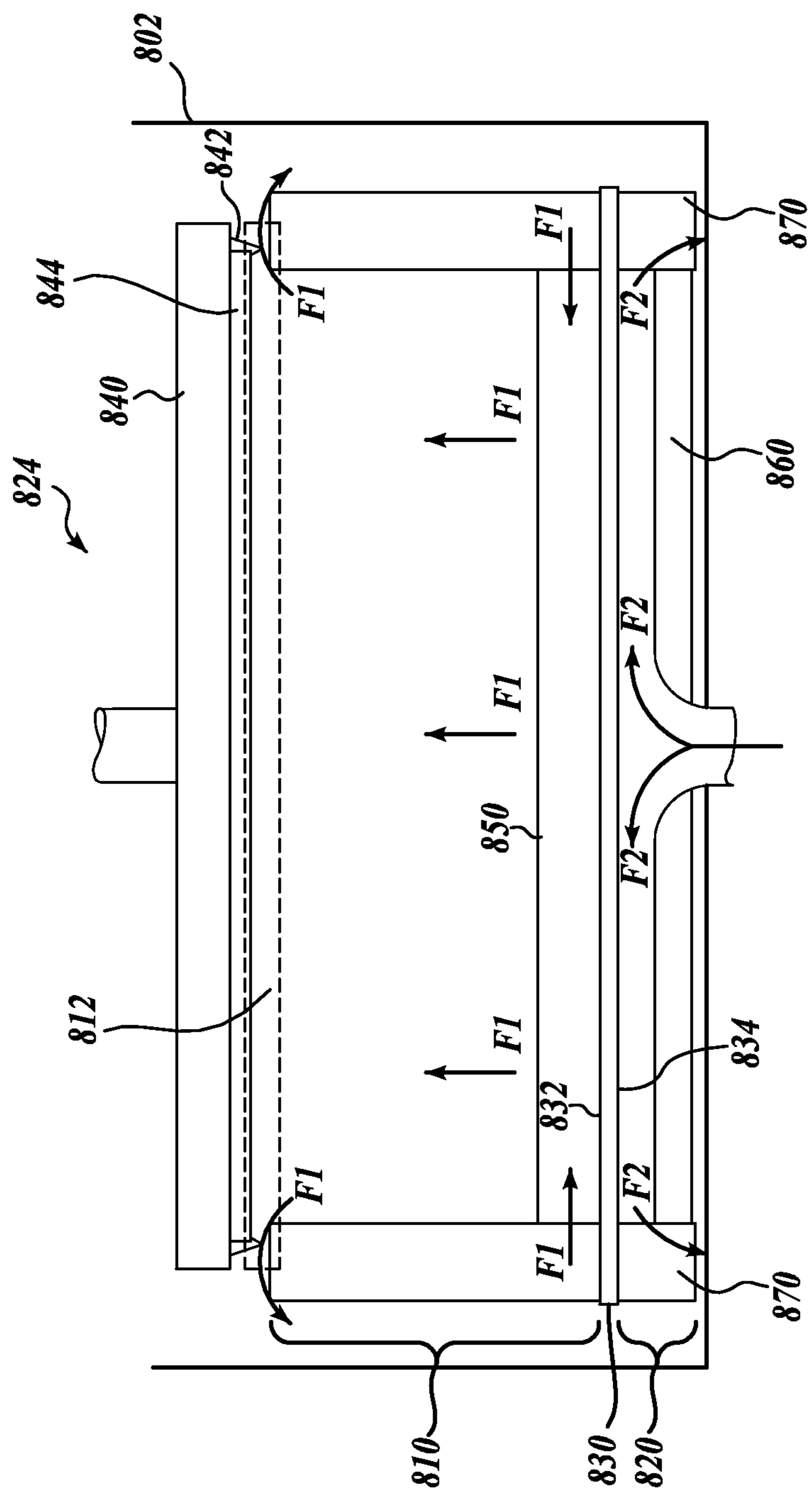


Fig. 8.

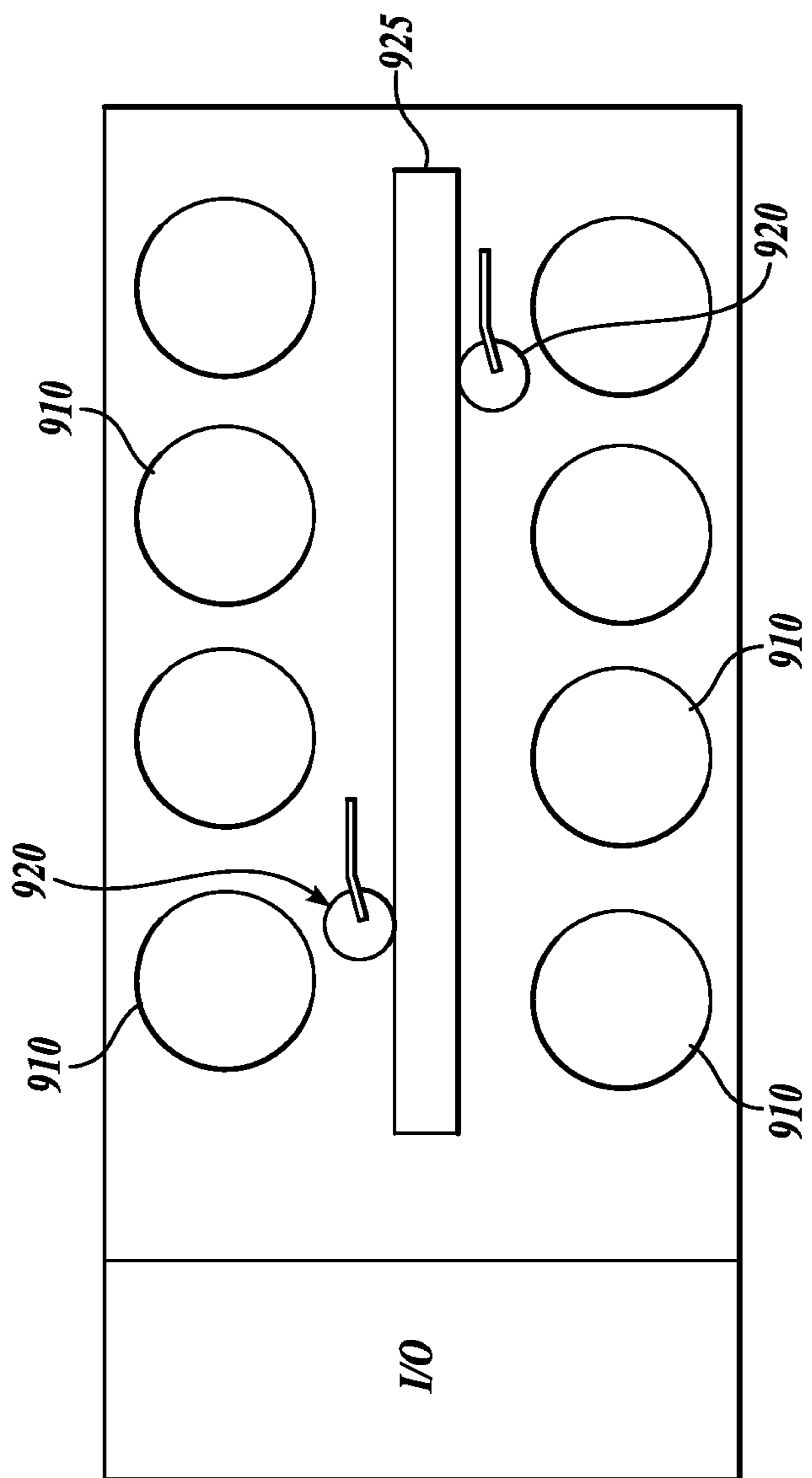


Fig. 9.

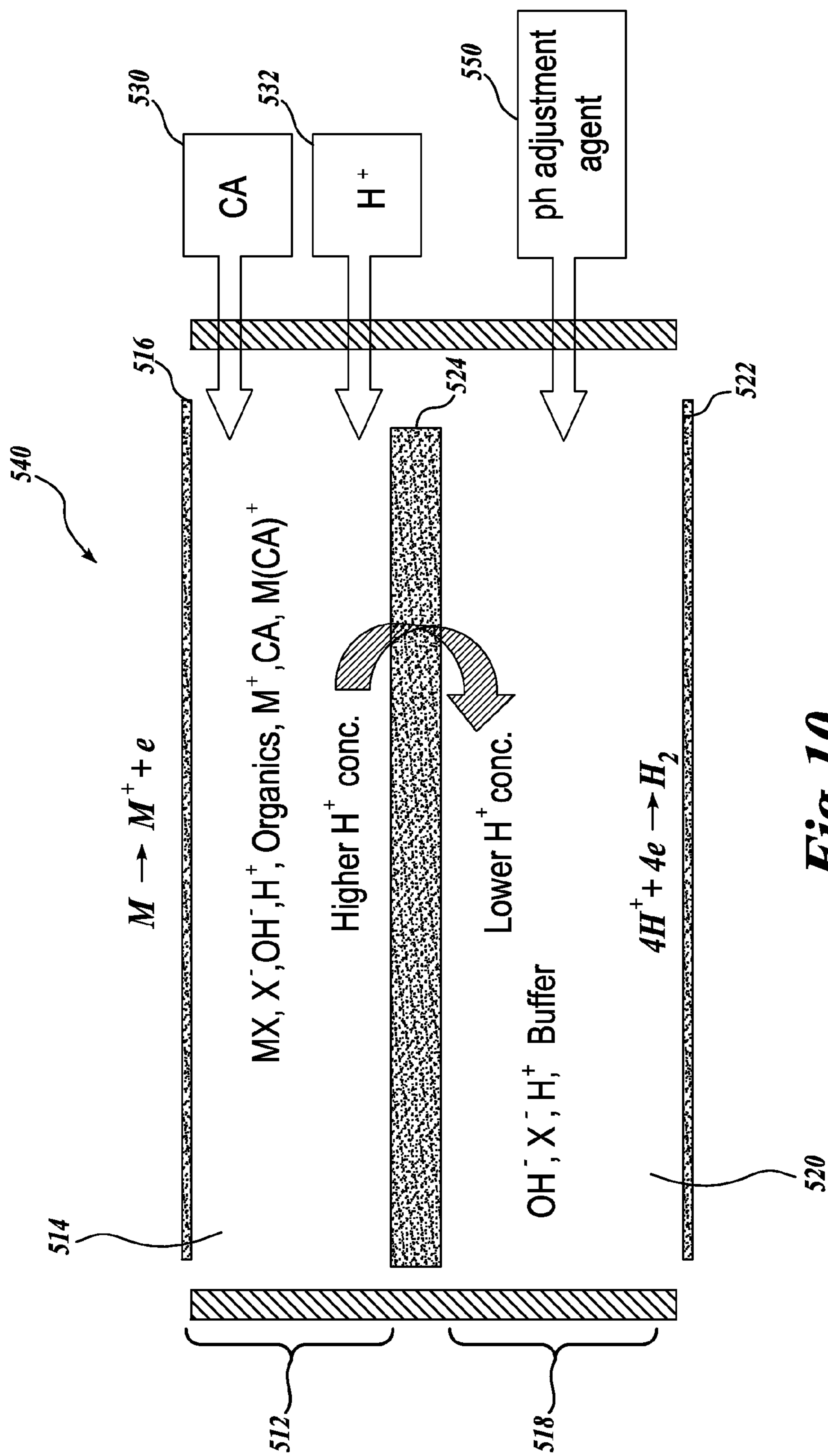


Fig. 10.

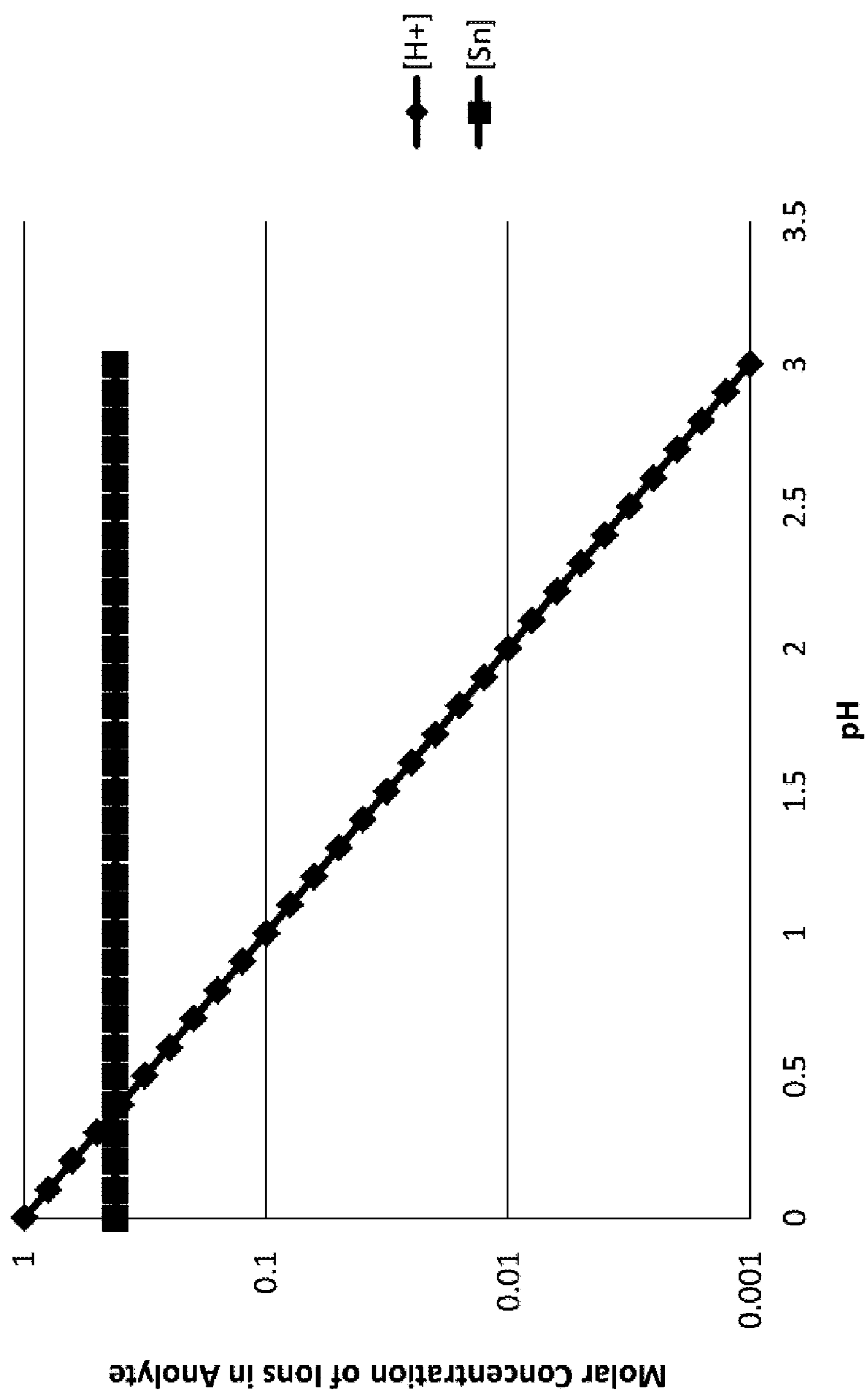


Fig. 11.

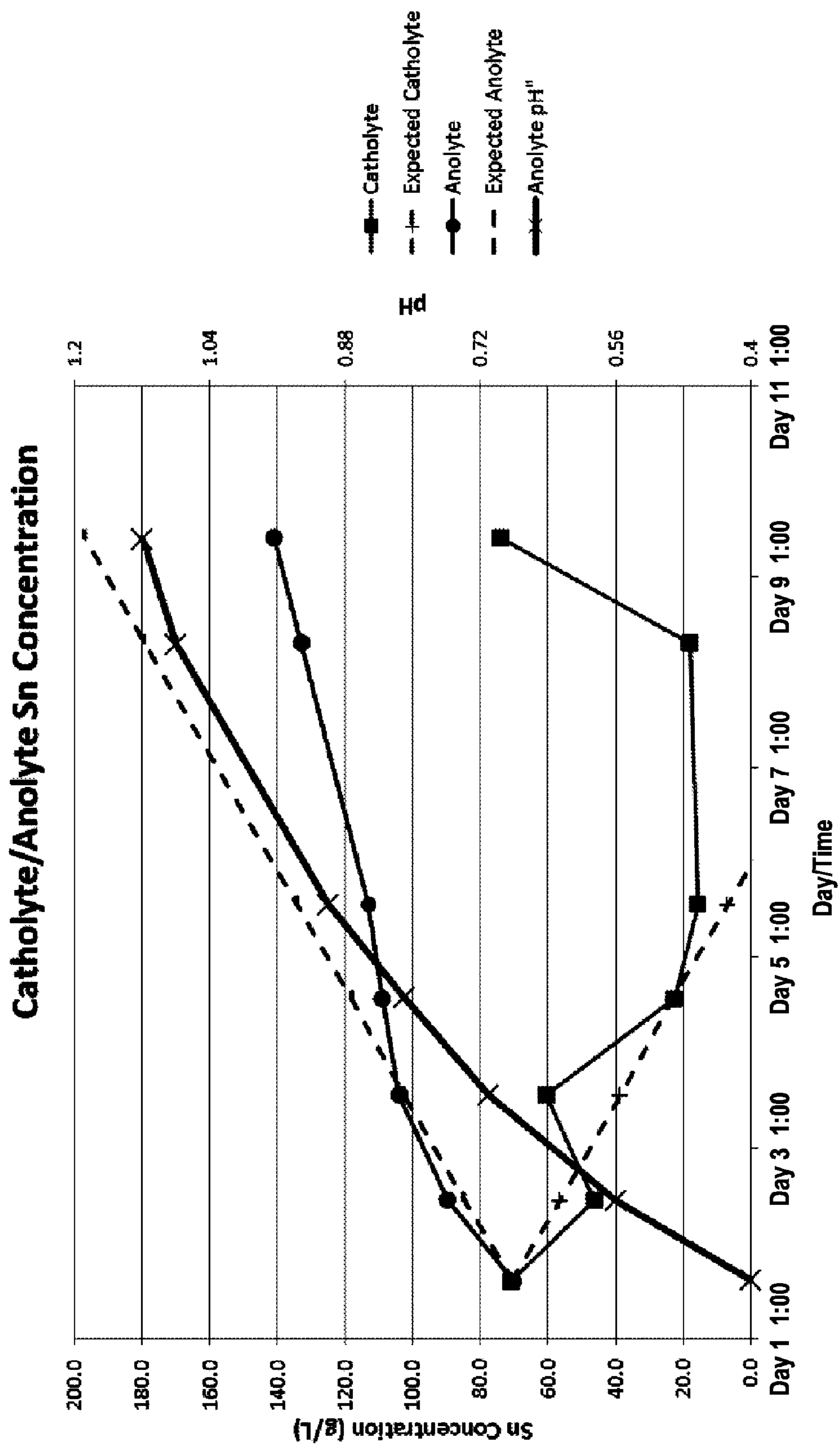


Fig. 12A.

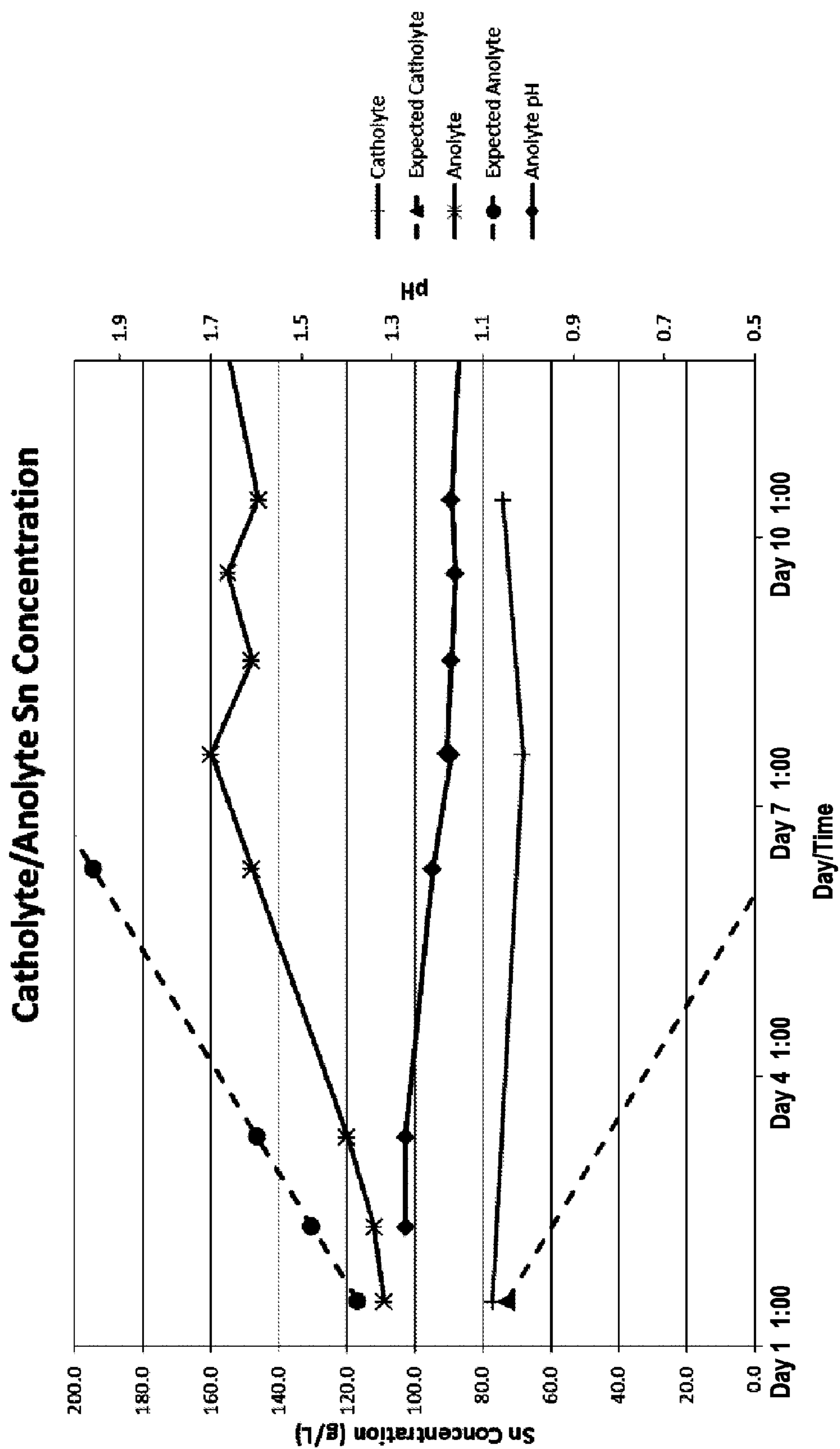


Fig. 12B.

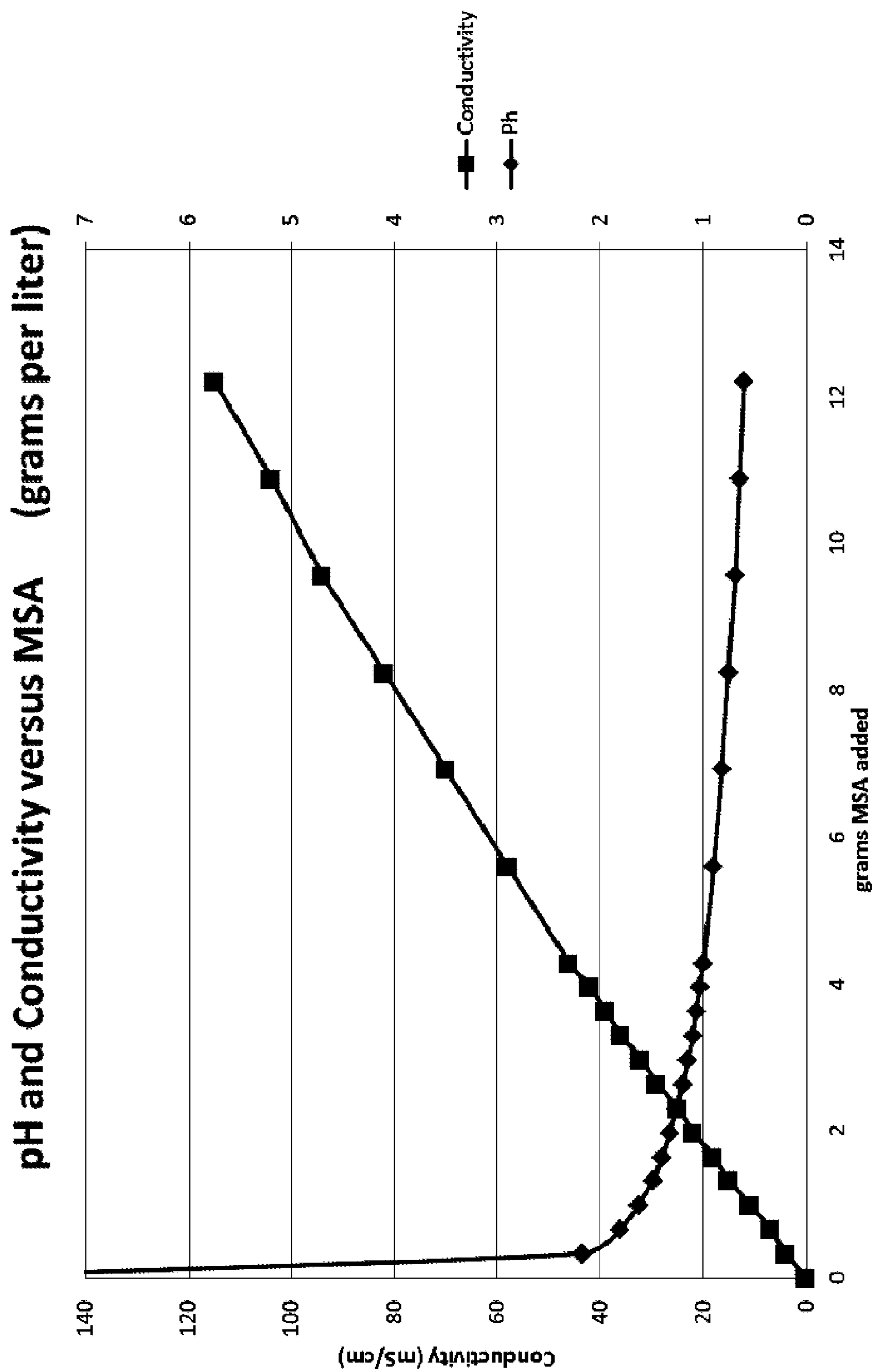


Fig. 13.

**METHODS FOR ELECTROCHEMICAL
DEPOSITION OF MULTI-COMPONENT
SOLDER USING CATION PERMEABLE
BARRIER**

CROSS-REFERENCES TO RELATED
APPLICATIONS

[0001] This application is continuation-in-part of U.S. patent application Ser. No. 13/559,494, filed Jul. 26, 2012, which is a continuation of U.S. patent application Ser. No. 11/414,145, filed Apr. 28, 2006, now U.S. Pat. No. 8,236,159, which is a continuation-in-part of U.S. application Ser. No. 10/861,899, filed Jun. 3, 2004, now U.S. Pat. No. 7,585,398; a continuation-in-part of U.S. application Ser. No. 10/729,357, filed Dec. 5, 2003, now U.S. Pat. No. 7,351,315; and a continuation-in-part of U.S. application Ser. No. 10/729,349, filed Dec. 5, 2003, now U.S. Pat. No. 7,351,314, the disclosures of which are hereby incorporated by reference herein in their entirety.

TECHNICAL FIELD

[0002] Embodiments of the present invention relate to electrolytic processing of microfeature workpieces and electrolytic treatment processes that utilize a cation permeable barrier.

BACKGROUND

[0003] Microfeature devices, such as semiconductor devices, imagers, displays, thin film heads, micromechanical components, microelectromechanical systems (MEMS), and large through-wafers vias are generally fabricated on and/or in microfeature workpieces using a number of machines that deposit and/or etch materials from the workpieces. Many current microfeature devices require interconnects and other very small, submicron sized features (e.g., 45-250 nanometers) formed by depositing materials into small trenches or holes. One particularly useful process for depositing materials into small trenches and/or vias is electrolytic processing, e.g., electroplating. Typical electrolytic processing techniques include electroplating processes that deposit copper, nickel, lead, gold, silver, tin, platinum, and other materials onto microfeature workpieces and etching processes that remove metals from microfeature workpiece surfaces.

[0004] In certain electroplating or etching processes, chelants or complexing agents are used to affect the electric potential at which metal ions are deposited onto or removed from surfaces of microfeature workpieces. Other components that may be present in the processing fluids include accelerators, suppressors, and levelers which can affect the results of the electroplating or electroetching process. Although these types of materials can positively influence the electroplating or electroetching processes, their use is not without drawbacks. For example, it is possible for these components to have an adverse impact on the electrolytic process as a result of reactions or other interactions with electrodes used in the electrolytic process.

[0005] Another challenge in depositing metals into narrow, deep trenches or vias is that it is difficult to completely fill the small features without creating voids or other nonuniformities in the deposited metal. For example, when depositing metal into a trench having a critical dimension of 45 nanometers to 250 nanometers, an ultrathin seed layer may be used, but care must be taken to ensure sufficient vacant space in the

trench for the subsequently deposited bulk metal. In addition, ultrathin seed layers may be problematic because the quality of the deposited seed layer may not be uniform. For example, ultrathin seed layers may have voids or other nonuniform physical properties that can result in nonuniformities in the material deposited onto the seed layer. Such challenges may be overcome by enhancing the seed layers or forming a seed layer directly on a barrier layer to provide competent seed layers that are well suited for depositing metals into trenches or holes with small critical dimensions. One technique for enhancing the seed layer or forming a seed layer directly on a barrier layer is to electroplate a material using a processing solution with a low conductivity. Such low conductivity processing fluids have relatively low hydrogen ion (H⁺) concentrations, i.e., relatively high pH. Suitable electrochemical processes for forming competent seed layers using low conductivity processing fluids are disclosed in U.S. Pat. No. 6,197,181, which is herein incorporated by reference.

[0006] Electroplating onto seed layers or electroplating materials directly onto barrier layers using low conductivity/high pH processing fluids presents additional challenges. For example, inert anodes are generally required when high pH processing fluids are used because the high pH tends to passivate consumable anodes. Such passivation may produce metal hydroxide particles and/or flakes that can create defects in the microfeatures. Use of inert anodes is not without its drawbacks. The present inventors have observed that when inert anodes are used, the resistivity of the deposited material increases significantly over a relatively small number of plating cycles. One way to combat this increase in the resistivity of the deposited material is to frequently change the processing fluid; however, this solution increases the operating cost of the process.

[0007] As a result, there is a need for electrolytic processes for treating microfeature workpieces that reduce adverse impacts created by the presence of complexing agents and/or other additives and also maintain deposit properties, such as resistivity, within desired ranges.

[0008] In wafer level packaging (WLP) electrochemical deposition (ECD), near eutectic tin-silver (Sn—Ag) is currently the alloy of choice for lead-free solder bumping and copper pillar capping. In current tin-silver plating processes, a liquid tin ion doping concentrate is added to the catholyte to replenish the tin ions consumed in the deposition process. However, tin ion concentrate tends to be more significantly more expensive than solid tin, and because of additives in the concentrate, results in reduced control over the stability and the lifetime of the catholyte.

[0009] Therefore, there exists a need for an electrochemical deposition method for plating more than one metal onto a microfeature workpiece, for example, as a multi-component solder, that uses a source of primary ions that is easier to control than a liquid doping concentrate added to the catholyte. Embodiments of the present disclosure are directed to fulfilling this and other needs.

SUMMARY

[0010] The embodiments described herein relate to processes for electrolytically processing a microfeature workpiece to deposit or remove materials from surfaces of microfeature workpieces. The processes described herein are capable of producing deposits exhibiting properties, such as resistivity values, within desired ranges over an extended number of plating cycles. The embodiments described herein

also relate to processes that reduce the adverse impacts created by the presence of complexing agents and/or other additives in processing fluids used to electrolytically process a microfeature workpiece. In some embodiments, the described processes employ low conductivity/high pH processing fluids without suffering from the drawback of defect formation in the deposited material resulting from the presence of metal hydroxide particles or flakes present in processing fluids in contact with the microfeature workpiece. Processors of microfeature workpieces will find certain processes described herein desirable because the processes produce high yields of acceptable deposits without requiring costly frequent replacement of processing fluids. Reducing adverse impacts created by the presence of complexing agents and/or other additives in the processing fluids may also be considered desirable by users of the electrolytic processes described herein.

[0011] In one embodiment, a surface of a microfeature workpiece is contacted with a first processing fluid that includes first processing fluid species, such as a cation, an anion, and a complexing agent. A counter electrode is in contact with a second processing fluid and an electrochemical reaction occurs at the counter electrode. The process effectively prevents movement of non-cationic, e.g., anionic species between the first processing fluid and the second processing fluid. In certain embodiments, the first processing fluid can be a low pH processing fluid, the second processing fluid can be a high pH processing fluid, the cation can be a metal ion to be deposited onto the surface of the microfeature workpiece, and the counter electrode can be an inert electrode.

[0012] In another embodiment, a surface of a microfeature workpiece is contacted with a first processing fluid that includes a metal ion to be deposited onto the surface of the microfeature workpiece. In addition, the first processing fluid includes a complexing agent and a counter anion to the metal ion. An inert anode is in contact with a second processing fluid, and an oxidizing agent is produced at the inert anode. The process employs a cation permeable barrier between the first processing fluid and the second processing fluid. The cation permeable barrier allows cations, e.g., hydrogen ions, to pass from the first processing fluid to the second processing fluid. In this embodiment, metal ions in the first processing fluid are deposited onto the surface of the microelectronic workpiece. In certain embodiments, the first and second processing fluids can be high pH processing fluids.

[0013] In a further embodiment, a surface of a microfeature workpiece is contacted with a first processing fluid that includes a metal ion to be deposited onto a surface of the microelectronic workpiece. In this embodiment, an inert anode is in contact with a second processing fluid that includes a buffer and pH adjustment agent and a cation permeable barrier is located between the first processing fluid and the second processing fluid.

[0014] The processes summarized above can be carried out in a system for electrolytically processing a microfeature workpiece. The system includes a chamber that has a processing unit for receiving a first processing fluid and counter electrode unit for receiving a second processing fluid. A counter electrode is located in the counter electrode unit, and a cation permeable barrier is located between the processing unit and the counter electrode unit. The system also includes a source of complexing agent. The chamber further includes a source of metal ion in fluid communication with the pro-

cessing unit or the counter electrode unit and a source of a pH adjustment agent in fluid communication with the processing unit.

[0015] Through the use of processes described above and the system described above, metals such as copper, nickel, lead, gold, silver, tin, platinum, ruthenium, rhodium, iridium, osmium, rhenium, and palladium can be deposited onto surfaces of a microfeature workpiece. Such surfaces can take the form of seed layers or barrier layers.

[0016] The process embodiments and systems described above can be used to electroplate materials onto a surface of a microfeature workpiece or used to electroetch or deplate materials from a surface of a microfeature workpiece. When the process is used to electroplate materials, the microfeature workpiece will function as a cathode, and the counter electrode will function as an anode. In contrast, when deplating is carried out, the microfeature workpiece will function as an anode, and the counter electrode will function as a cathode.

[0017] Accordingly, in another embodiment, a surface of a microfeature workpiece is contacted with a first processing fluid that includes hydrogen ion and a counter ion to a metal on the surface. A cathode is contacted with a second processing fluid also containing hydrogen ion, and a cation permeable barrier is located between the first processing fluid and the second processing fluid. Chemical species in the second processing fluid are reduced, and an acid is introduced to the first processing fluid to provide hydrogen ions. Hydrogen ions from the first processing fluid are passed through the cation permeable barrier to the second processing fluid. In accordance with this embodiment, metals from the surface of the microfeature workpiece are electrolytically dissolved, i.e., oxidized and deplated.

[0018] The process summarized in the previous paragraph can be carried out in a system for electrolytically processing a microfeature workpiece that includes a chamber that has a processing unit for receiving a first processing fluid and a counter electrode unit for receiving a second processing fluid. A cation permeable barrier is positioned between the processing unit and the counter electrode unit. The system further includes a cathode in the counter electrode unit, a source of hydrogen ions in fluid communication with the processing unit, and a source of pH adjustment agent in fluid communication with the counter-electrode unit.

[0019] Through the use of the processes and systems described above for removing materials from surfaces of a microfeature workpiece, metals such as copper, nickel, lead, gold, silver, tin, and platinum can be deplated from a microfeature workpiece surface.

[0020] In accordance with another embodiment of the present disclosure, a process for electrolytically processing a microfeature workpiece as the working electrode with a first processing fluid and a counter electrode is provided. The process generally includes contacting a surface of the microfeature workpiece with the first processing fluid, the first processing fluid comprising first processing fluid species including at least one metal cation, an anion, and a complexing agent. The process further includes contacting the counter electrode with a second processing fluid, producing an electrochemical reaction at the counter electrode, and electrolytically depositing the metal cation onto the surface of the microfeature workpiece. The process further includes substantially preventing movement of anionic and complexing agent species between the first processing fluid and the second processing fluid.

[0021] In accordance with another embodiment of the present disclosure, a process for electrolytically processing a microfeature workpiece as the working electrode with a first processing fluid and a counter electrode is provided. The process generally includes contacting a surface of the microfeature workpiece with the first processing fluid, the first processing fluid comprising first processing fluid species including at least one metal cation, an anion, and at least one organic component selected from the group consisting of accelerators, suppressors, and levelers. The process further includes contacting the counter electrode with a second processing fluid, producing an electrochemical reaction at the counter electrode, and electrolytically depositing the metal cation onto the surface of the microfeature workpiece. The process further includes providing a cation exchange membrane to substantially prevent movement of anionic species and the at least one organic component between the first processing fluid and the second processing fluid.

[0022] In accordance with yet another embodiment of the present disclosure, a process for electrolytically processing a microfeature workpiece as the working electrode with a first processing fluid and a counter electrode is provided. The process includes contacting a surface of the microfeature workpiece with the first processing fluid, the first processing fluid comprising first processing fluid species including a metal cation, an anion, and a complexing agent. The process further includes contacting the counter electrode with a second processing fluid, producing an electrochemical reaction at the counter electrode, and electrolytically depositing the metal cation onto the surface of the microfeature workpiece. The process further includes providing a cation permeable barrier between the first processing fluid and the second processing fluid to substantially prevent the movement of anionic and complexing agent species between the first processing fluid and the second processing fluid, wherein the cation permeable barrier is oriented in a substantially horizontal configuration.

[0023] In accordance with another embodiment of the present disclosure, a process for electrolytically processing a microfeature workpiece as the working electrode in a first processing fluid and a counter electrode in a second processing fluid is provided. The process generally includes: contacting a surface of the microfeature workpiece with the first processing fluid, the first processing fluid including at least a first metal cation; contacting the counter electrode with a second processing fluid, the second processing fluid including a second metal cation; allowing the second metal cation to move from the second processing fluid to the first processing fluid, but substantially preventing movement of the first metal cation from the first processing fluid to the second processing fluid by providing a cation permeable barrier between the first processing fluid and the second processing fluid, wherein the primary mass transport of the second metal cation from the second processing fluid to the first processing fluid is across the cation permeable barrier; and electrolytically depositing the first and second metal cations onto the surface of the microfeature workpiece.

[0024] In accordance with another embodiment of the present disclosure, a process for electrolytically processing a microfeature workpiece as the working electrode with a first processing fluid and a counter electrode is provided. The process includes: contacting a surface of the microfeature workpiece with the first processing fluid, the first processing fluid comprising first processing fluid species including at

least a first metal cation; contacting the counter electrode with a second processing fluid; producing an electrochemical reaction at the counter electrode to produce a second metal cation in the second processing fluid; providing a cation exchange membrane to allow the second metal cation to move from the second processing fluid to the first processing fluid, but to substantially prevent movement of the first metal cation from the first processing fluid to the second processing fluid when electrolytically processing the microfeature workpiece; and separating the second processing fluid from the membrane when not electrolytically processing the microfeature workpiece.

[0025] In accordance with another embodiment of the present disclosure, a process for electrolytically processing a microfeature workpiece as the cathode with a first processing fluid and an anode is provided. The process generally includes: contacting a surface of the microfeature workpiece with the first processing fluid, the first processing fluid comprising first processing fluid species including at least a first metal cation; contacting the anode with a second processing fluid; consuming the anode to produce a second metal cation in the second processing fluid; providing a cation exchange membrane to allow the second metal cation to move from the second processing fluid to the first processing fluid, but to substantially prevent movement of the first metal cation from the first processing fluid to the second processing fluid, wherein the second processing fluid is not dosed in the first processing fluid; and electrolytically depositing the first and second metal cations onto the surface of the microfeature workpiece.

[0026] In accordance with any of the process described herein, the cation permeable barrier may be a cation exchange membrane.

[0027] In accordance with any of the process described herein, the process may further comprise producing an electrochemical reaction at the counter electrode to produce the second metal cation.

[0028] In accordance with any of the process described herein, the working electrode may be a cathode, and the counter electrode may be an anode.

[0029] In accordance with any of the process described herein, the first processing fluid may be dosed with the first metal cation.

[0030] In accordance with any of the process described herein, the counter electrode may be a consumable electrode.

[0031] In accordance with any of the process described herein, either or both of the first and second processing fluids may be dosed with the second metal cation.

[0032] In accordance with any of the process described herein, dosing in either or both of the first and second processing fluids with the second metal cation may not be the major source of the second metal cation in the first processing fluid.

[0033] In accordance with any of the process described herein, the first metal cation concentration in the first processing fluid may be in the range of about 0.1 g/L to about 5.0 g/L.

[0034] In accordance with any of the process described herein, the second metal cation concentration in the first processing fluid may be selected from the group consisting of in the range of about 40 to about 80 g/L, about 40 to about 120 g/L, and about 40 to about 150 g/L.

[0035] In accordance with any of the process described herein, the pH of the second processing fluid may be higher than the pH of the first processing fluid.

[0036] In accordance with any of the process described herein, the pH of the second processing fluid may be selected from the group consisting of about 1.0 to about 2.0, about 1.2 to about 1.8, about 1.5 to about 2.2, greater than about 2.0, about 1.0 to about 3.0, and about 2.0 to about 3.0.

[0037] In accordance with any of the process described herein, the pH of the first processing fluid may be selected from the group consisting of less than or equal to 1.0 and less than or equal to 0.5, and in the range of 0 to 1.0.

[0038] In accordance with any of the process described herein, the first metal cation may be selected from the group consisting of copper ion, lead ion, gold ion, tin ion, silver ion, bismuth ion, indium ion, platinum ion, ruthenium ion, rhodium ion, iridium ion, osmium ion, rhenium ion, palladium ion, and nickel ion.

[0039] In accordance with any of the process described herein, the second metal cation may be selected from the group consisting of copper ion, lead ion, tin ion, bismuth ion, indium ion, silver ion, platinum ion, ruthenium ion, rhodium ion, iridium ion, osmium ion, rhenium ion, palladium ion, and nickel ion.

[0040] In accordance with any of the process described herein, the process may further include depositing a third metal cation selected from the group consisting of copper ion, lead ion, gold ion, tin ion, silver ion, bismuth ion, indium ion, platinum ion, ruthenium ion, rhodium ion, iridium ion, osmium ion, rhenium ion, palladium ion, nickel ion.

[0041] In accordance with any of the process described herein, the process may further include depositing a co-deposited metal.

[0042] In accordance with any of the process described herein, the first processing fluid may include an antioxidant.

[0043] In accordance with any of the process described herein, the second processing fluid may include an antioxidant.

[0044] In accordance with any of the process described herein, where the second processing fluid may not be dosed into the first processing fluid.

BRIEF DESCRIPTION OF THE DRAWINGS

[0045] The foregoing aspects and many of the attendant advantages of the processes described herein will become more readily appreciated as the same become better understood by reference to the following detailed description, when taken in conjunction with the accompanying drawings, wherein:

[0046] FIG. 1 is a schematic illustration of a reactor for carrying out processes described herein;

[0047] FIG. 2 is a schematic illustration of the chemistry and chemical reactions occurring in one embodiment of the processes for electroplating a metal using an inert anode described herein;

[0048] FIG. 3 is a schematic illustration of the chemistry and chemical reactions occurring in another embodiment of the processes for electroplating a metal using a consumable anode described herein;

[0049] FIGS. 4A-4C are schematic illustrations of one embodiment of the processes described herein for electrolytically treating a seed layer;

[0050] FIGS. 5A and 5B are schematic illustrations of one embodiment of the processes described herein for electrolytically treating a barrier layer;

[0051] FIG. 6 is a schematic illustration of the chemistry and chemical reactions occurring in one embodiment of the processes for electroplating two metals described herein using an inert anode;

[0052] FIG. 7 is a schematic illustration of the chemistry and chemical reactions occurring in one embodiment of the processes for electroplating two metals described herein using a consumable anode;

[0053] FIG. 8 is a schematic illustration of a reactor for carrying out processes described herein;

[0054] FIG. 9 is a schematic illustration of a tool that includes chambers for carrying out processes described herein;

[0055] FIG. 10 is a schematic illustration of the chemistry and chemical reactions occurring in one embodiment of the processes for deplating a metal described herein;

[0056] FIG. 11 is a graphical representation of the relationship between the molar concentration of tin ions in the anolyte and the pH of the anolyte;

[0057] FIGS. 12A and 12B are graphical representations of the relationship between pH and tin concentration in the catholyte and the anolyte; and

[0058] FIG. 13 is a graphical representation of the relationship between the pH and conductivity of the anolyte in view of MSA concentration.

DETAILED DESCRIPTION

[0059] As used herein, the terms “microfeature workpiece” or “workpiece” refer to substrates on and/or in which micro devices are formed. Such substrates include semiconductive substrates (e.g., silicon wafers and gallium arsenide wafers), nonconductive substrates (e.g., ceramic or glass substrates), and conductive substrates (e.g., doped wafers). Examples of micro devices include microelectronic circuits or components, micromechanical devices, microelectromechanical devices, micro optics, thin film recording heads, data storage elements, microfluidic devices, and other small scale devices.

[0060] In the description that follows regarding electroplating a metal onto a microfeature workpiece, specific reference is made to copper as an example of a metal ion that can be electroplated onto a microfeature workpiece. The reference to copper ions is for exemplary purposes, and it should be understood that the following description is not limited to copper ions. Examples of other metal ions useful in the processes described herein include gold ions, tin ions, silver ions, platinum ions, lead ions, cobalt ions, zinc ions, nickel ions, ruthenium ions, rhodium ions, iridium ions, osmium ions, rhenium ions, and palladium ions.

[0061] In the description that follows regarding electroplating more than one metal onto a microfeature workpiece, specific reference is made to a tin-silver solder system as an example of metal ions that can be electroplated onto a microfeature workpiece to form a composite deposit. The reference to deposition of a tin-silver solder is for exemplary purposes, and it should be understood that the description is not limited to tin and silver ions.

[0062] With respect to the description that follows regarding deplating a metal from a microfeature workpiece, specific reference is made to copper as an example of a metal ion that can be deplated from a microfeature workpiece. The reference to copper is for exemplary purposes, and it should be understood that the description regarding deplating are not limited to the removal of copper. Examples of other metals that can be removed from a microfeature workpiece in accor-

dance with embodiments described herein include gold ions, tin ions, silver ions, platinum ions, lead ions, cobalt ions, zinc ions, nickel ions, ruthenium ions, rhodium ions, iridium ions, osmium ions, rhenium ions, and palladium ions.

[0063] Processes described herein can be carried out in an electroplating or deplating reactor, such as the one described below with reference to FIG. 1. Referring to FIG. 1, electrochemical deposition chamber 400 includes an upper processing unit 404 containing a first processing fluid 406 (e.g., a catholyte in an electroplating process or an anolyte in a deplating process) and a counter electrode unit 410 below the processing unit 404 that contains a second processing fluid 412 (e.g., anolyte in an electroplating process or a catholyte in a deplating process) which may be different in composition and/or properties from the first processing fluid 406. Processing unit 404 receives a working electrode 408 (e.g., a microfeature workpiece) and delivers first processing fluid 406 to the working electrode 408. Counter electrode unit 410 includes a counter electrode 414 that is in contact with the second processing fluid 412. When copper is to be deposited onto working electrode 408, working electrode 408 is the cathode and counter electrode 414 is the anode. Accordingly, in plating application, first processing fluid 406 is a catholyte, and second processing fluid 412 is an anolyte. The catholyte 406 typically contains components in the form of ionic species such as acid ions and metal ions, as described below in more detail.

[0064] In general, the catholyte contains components in the form of ionic species, such as acid ions (e.g., H^+), hydroxyl ions, and metal ions, and complexing agent(s) capable of forming a complex with the metal ions. The catholyte may also include organic components, such as accelerators, suppressors, and levelers that improve the results of the electroplating process. In addition, the catholyte may include a pH adjustment agent to affect the pH of the catholyte. The anolyte generally includes ionic species as well, such as acid ions (e.g., H^+), hydroxyl ions, and metal ions. The catholyte may also include a pH adjustment agent. Additional details regarding the various components in the catholyte and anolyte are provided below.

[0065] When copper is to be deplated from working electrode 408, working electrode 408 is the anode, and counter electrode 414 is the cathode. Accordingly, in deplating applications, the first processing fluid 406 is an anolyte, and the second processing fluid 412 is a catholyte.

[0066] Reactor 400 also includes a nonporous cation permeable barrier 402 between first processing fluid 406 and the second processing fluid 412. Nonporous cation permeable barrier 402 allows cations (e.g., H^+ and Cu^{2+}) to pass through the barrier while inhibiting or substantially preventing non-cationic components, such as organic components (e.g., accelerators, suppressors, and levelers) and anionic components from passing between the first and second processing fluids. By inhibiting or substantially preventing non-cationic components from passing between the first processing fluid 406 and second processing fluid 412, adverse effects on the deposited material resulting from the presence of unwanted non-cationic components, such as unwanted anions or organic bath components, in the first processing fluid 406 can be avoided. As such, nonporous cation permeable barrier 402 separates first processing fluid 406 and second processing fluid 412 such that first processing fluid 406 can have different chemical characteristics and properties than second processing fluid 412. For example, the chemical components of first

processing fluid 406 and second processing fluid 412 can be different, the pH of first processing fluid 406 and second processing fluid 412 can be different, and concentrations of components common to both first processing fluid 406 and second processing fluid 412 can be different.

[0067] In the following description of a copper electroplating process, for consistency, working electrode 408 will be referred to as the cathode, and counter electrode 414 will be referred to as the anode. Likewise, first processing fluid 406 will be referred to as the catholyte, and second processing fluid 412 will be referred to as the anolyte. When reactor 400 is used to electrolytically process a microfeature workpiece to deposit metal ions thereon, an electric potential is applied between anode 414 and cathode 408. Copper ions in the catholyte are consumed by the deposition of copper ions onto the cathode. Meanwhile, the anode becomes positively charged and attracts negatively charged ions to its surface. For example, hydroxyl ions in the anolyte are attracted to the anode where they react to liberate oxygen and produce water. The foregoing results in a gradient of charge in the anolyte with unbalanced positively charged species in the anolyte solution, and negatively charged species in the catholyte solution. This charge imbalance encourages the transfer of positively charged cations through the cation permeable barrier 402 from anolyte 412 to the catholyte 406. An electrochemical reaction (e.g., losing or gaining electrons) occurs at cathode 408, resulting in metal ions being reduced (i.e., gaining electrons) to metal on surfaces of cathode 408.

[0068] Reactor 400 effectively maintains the concentration of metal ions in catholyte 406 during the electroplating process in the following manner. As metal ions are deposited onto the surface of cathode 408, in addition to the metal ions passing from the anolyte 412 to the catholyte 406, additional metal ions can be introduced to catholyte 406 from a source of metal ions 130, which is in fluid communication with processing unit 404. As explained below in more detail, these metal ions can be provided by delivering a metal salt solution to processing unit 404. Processing unit 404 can also be in fluid communication with sources of other components that need replenishment. In a similar fashion, counter electrode unit 410 may be in fluid communication with sources of components that require replenishment. For example, counter electrode unit 410 can be in fluid communication with a source of pH adjustment agent 132. Likewise, both processing unit 404 and electrode unit 410 can include conduits or other structures for removing portions of catholyte 406 from processing unit 404 or portions of anolyte 412 from counter electrode unit 410.

[0069] Anode 414 may be a consumable anode or an inert anode. Exemplary consumable anodes and inert anodes are described below in more detail.

[0070] Cation permeable barrier 402 provides several advantages by substantially preventing certain anionic species and organic components from migrating between the catholyte and the anolyte. For example, organic components from the catholyte are unable to flow past the anode and decompose into products that may interfere with the plating process. Second, because organic components do not pass from the catholyte to the anolyte, they are consumed at a slower rate so that it is less expensive and easier to control the concentration of organic components in the catholyte. Third, the risk of passivation by reaction of the anode with organic components is reduced or eliminated. In addition, the presence of the cation permeable barrier reduces the chances that

metal flakes or small particles resulting from anode passivation (when a consumable anode is used in combination with a high pH, low conductivity, low acid anolyte) reach the workpiece where the flakes or particles may adversely impact the deposited metal. Another benefit of using the cation membrane is that gases generated at the anode are prevented from passing into the catholyte where they may contact with the workpiece surface.

[0071] Exemplary chemistries present in processing unit 404 in FIG. 1 and counter electrode unit 410 of FIG. 1 are described below with reference to FIG. 2. It should be understood that by describing chemical reactions that are believed to occur within reactor 400, the processes described herein are not limited to processes wherein these reactions occur.

[0072] FIG. 2 schematically illustrates an example of the operation of reactor 400 using a cation permeable barrier 422 and an inert anode 424 in combination with a low conductivity/high pH catholyte 426 and a low conductivity/high pH anolyte 428. In the description that follows, catholyte 426 in processing unit 430 contains a metal ion (M^+), e.g., copper ion (Cu^{2+}), a counter ion (X^-) for the metal ion, e.g., sulfate ion (SO_4^{2-}), a complexing agent (CA), chelated with the metal ions, a pH buffer such as boric acid (H_3BO_3) that dissociates into hydrogen ions (H^+) and $H_2BO_3^-$ and a pH adjustment agent, such as tetramethylammonium hydroxide (TMAH) that dissociates into hydroxyl ion (OH^-) and TMATM. The specific hydrogen ion concentration and pH of catholyte 426 can be chosen taking into consideration conventional factors such as complexing ability of the complexing agent, buffering capability of the buffer, metal ion concentrations, volatile organics concentrations, deposition potential of the complex at the particular pH, solubility of the catholyte constituents, stability of the catholyte, desired characteristics of the deposits, and diffusion coefficients of the metal ions. Low conductivity, low acid anolyte 428 in electrode unit 432 includes an aqueous solution of an acid, e.g., sulfuric acid that dissociates into hydrogen ion (H^+) and sulfate ions (SO_4^{2-}). Anolyte 428 may also include a buffer. The hydrogen ion concentration of anolyte 428 is preferably greater than the hydrogen ion concentration of catholyte 426, although this is not required as explained below in more detail. This differential encourages the movement of hydrogen ions from the anolyte 428 to the catholyte 426. In order to account for this increasing hydrogen ion concentration in catholyte 426, pH adjustment agents can be added to catholyte 426. Hydrogen ions from anolyte 428 that migrate across cation permeable barrier 422 to catholyte 426 are replenished in anolyte 428 by the oxidation of water at anode 424, which produces hydrogen ions.

[0073] During a plating cycle, an electric potential is applied between cathode 434 and inert anode 424. As metal ions are reduced and electroplated onto cathode 434, hydrogen ions (H^+) accumulate in the anolyte 428 near a first surface 436 of cation permeable barrier 422. The resulting electrical charge gradient and concentration gradient causes the positively charged hydrogen ions to move from first surface 436 of cation permeable barrier 422 to the second surface 438 of cation permeable barrier 422 that is in contact with catholyte 426. The transfer of positively charged hydrogen ions from anolyte 428 to catholyte 426 during the plating cycle maintains the charge balance of reactor 400. The electrical charge gradient created by applying an electric potential between cathode 434 and anode 424 also hinders the migration of cations, e.g., metal ions M^+ and cations of pH adjust-

ment agent from transferring from catholyte 426 to anolyte 428 through cation permeable barrier 422. In order to avoid the build up of counter ions (X^-) of the metal ions and cations of the pH adjustment agent in the catholyte, these ionic and cationic species can be removed from the catholyte 426.

[0074] Continuing to refer to FIG. 2, during a plating cycle, as explained above, metal ions in catholyte 426 are reduced at cathode 434 and are deposited as metal. Metal ions that are consumed by the electroplating are replenished by the addition of a solution of metal salt (MX) to catholyte 426.

[0075] While operating reactor 400 with the hydrogen ion concentration of anolyte 428 greater than the hydrogen ion concentration of catholyte 426 is preferred in order to promote transfer of hydrogen ions from the anolyte 428 to catholyte 426 through cation permeable membrane 422, it is also possible to operate reactor 400 with the hydrogen ion concentration of the anolyte 428 being less than the hydrogen ion concentration in the catholyte 426. Providing such a hydrogen ion concentration gradient would reduce the driving force promoting transport of hydrogen ions from anolyte 428 to catholyte 426 in favor of the transport of other cationic species that may be present in catholyte 426 in order to provide the necessary charge balance. The transport of such metal cations from catholyte 428 to anolyte 426 would be promoted by the electrical charge gradient between anode 424 and cathode 434. Under such circumstances, it may be necessary to add pH adjustment agents to anolyte 428 in order to maintain the hydrogen ion concentration in anolyte 428 below the hydrogen ion concentration of catholyte 426.

[0076] Metals may also be deposited using a cation permeable barrier and a consumable anode. Referring to FIG. 3, reactor 450, that includes a cation permeable barrier 452, a consumable anode 454, a low conductivity/high pH catholyte 456 and a low conductivity/high pH anolyte 458, is illustrated. For the embodiment of FIG. 3, catholyte 456 can have a composition that is similar to the composition of catholyte 426 described with reference to FIG. 2. Anolyte 458 includes hydrogen ions (H^+) and metal ions (M^+) from dissolution of consumable anode 454. Anolyte 458 can also include a buffer and dissociation products of pH adjustment agent. It is preferred that positively charged metal ions (M^+) transfer across cation permeable barrier 454 as opposed to positively charged hydrogen ions (H^+). Accordingly, it is preferred that anolyte 458 be a low acid/high pH anolyte so that there is an absence of a hydrogen ion concentration gradient between catholyte 456 and anolyte 458 that would promote the migration of the hydrogen ions from anolyte 458 to catholyte 456. Furthermore, by inhibiting the transfer of positively charged hydrogen ions from anolyte 458 to catholyte 456, a more constant catholyte pH can be maintained and the need to add a pH adjusting agent to the catholyte can be reduced. As noted above, this simplifies maintenance of the catholyte and helps to maintain the conductivity of the catholyte relatively stable during repeated plating cycles.

[0077] Continuing to refer to FIG. 3, during a plating cycle, an electric potential is applied between cathode 460 and anode 454. Metal is oxidized at anode 454 and metal ions (M^+) accumulate in the anolyte near a first surface 462 of cation permeable barrier 452. The resulting electrical charge gradient causes the positively charged metal cations (M^+) to move from the first surface 462 of cation permeable barrier 452 to the second surface 464 of cation permeable barrier 452. The transfer of positively charged metal ions from anolyte 458 to catholyte 456 during the plating cycle main-

tains the charge balance of reactor **450**. It should be understood that hydrogen ions will also transfer from anolyte **458** through cation exchange membrane **452** to catholyte **456**, the magnitude of such transport being dictated in part by the hydrogen ion concentration gradient between anolyte **458** and catholyte **456** as described above. During the plating cycle, metal ions (M^+) in catholyte **456** are reduced at cathode **460** and deposited as metal.

[0078] Microfeature workpieces that can be processed using processes described herein can include different structures on their surfaces that can be electrolytically processed to deposit materials thereon. For example, a semiconductor microfeature workpiece can include seed layers or barrier layers. Referring to FIGS. 4A-4C, one sequence of steps for electrolytically processing a seed layer using a process described herein is provided.

[0079] Referring to FIG. 4A, a cross-sectional view of a microstructure, such as trench **105** that is to be filled with bulk metallization is illustrated and will be used to describe use of processes described herein to enhance a seed layer. As shown, a thin barrier layer **110**, for example, titanium nitride or tantalum nitride, is deposited over the surface of a semiconductor device or, as illustrated in FIG. 4A, over a layer of dielectric **108** such as silicon dioxide. Any known technique such as chemical vapor deposition (CVD) or physical vapor deposition (PVD), can be used to deposit barrier layer **110**.

[0080] After deposition of barrier layer **110**, an ultrathin copper seed layer **115** is deposited on barrier layer **110**. The resulting structure is illustrated in FIG. 4B. Seed layer **115** can be formed using a vapor deposition technique also, such as CVD or PVD. Alternatively, seed layer **115** can be formed by direct electroplating onto barrier layer **110**. Owing to the small dimensions of trench **105**, techniques used to form ultrathin seed layer **115** should be capable of forming the seed layer without closing off small geometry trenches. In order to avoid closing off small geometry trenches, seed layer **115** should be as thin as possible while still providing a suitable substrate upon which to deposit bulk metal.

[0081] The use of ultrathin seed layer **115** introduces its own set of drawbacks. For example, ultrathin seed layers may not coat the barrier layer in a uniform manner. For example, voids or non-continuous seed layer regions on the sidewalls of the trenches such as at **120**, can be present in ultrathin seed layer **115**. The processes described herein can be used to enhance seed layer **115** to fill the void or non-continuous regions **120** found in ultrathin seed layer **115**. Referring to FIG. 4C, to achieve this enhancement, the microfeature workpiece is processed as described herein to deposit a further amount of metal **118** onto ultrathin seed layer **115** and/or portions of underlying barrier layer **110** that are exposed at voids or non-continuous portions **120**.

[0082] Preferably, this seed layer enhancement continues until a sidewall step coverage, i.e., the ratio of seed layer **115** thickness at the bottom sidewall regions to the nominal thickness of seed layer **115** at the exteriorly disposed side of the workpiece, achieves a value of at least 10%. More preferably, the sidewall step coverage is at least about 20%.

[0083] Preferably, such sidewall step coverage values are present in substantially all of the recessed structures of the microfeature workpiece; however, it will be recognized that certain recessed structures may not reach such sidewall step values.

[0084] Another type of feature on the surface of a microfeature workpiece that can be electrolytically treated using

processes described herein is a barrier layer. Barrier layers are used because of the tendency of certain metals to diffuse into silicon junctions and alter the electrical characteristics of semiconductor devices formed in a substrate. Barrier layers made of materials such as titanium, titanium nitride, tantalum, tantalum nitride, tungsten, and tungsten nitride are often laid over silicon junctions and any intervening layers prior to depositing a layer of metal. Referring to FIG. 5A, a cross-sectional view of a microstructure, such as trench **205** that is to be filled with bulk metallization is illustrated, and will be used to describe the formation of a metal layer directly onto a barrier layer using processes described herein. As illustrated in FIG. 5A, thin barrier layer **210** is deposited over the surface of a semiconductor device or, as illustrated in FIG. 5A, over a layer of dielectric **208**, such as silicon dioxide. Barrier layer **210** can be deposited as described above with reference to FIG. 4A using CVD or PVD techniques. After barrier layer **210** is deposited, the microfeature workpiece is processed as described herein to form a metal feature **215** over barrier layer **210**. The resulting structure can then be further processed to deposit bulk metal (not shown) to fill the trench **205**.

[0085] The pH of processing fluids described herein can vary from alkaline to acidic. The low conductivity/high pH processing fluids described herein are distinct from low pH ($\text{pH} < 7$) processing fluids such as acidic electroplating baths. The concentration of H^+ useful in high pH processing fluids may vary with those providing pHs above 7, preferably above 8 and most preferably above 9 being examples of useful high pH processing fluids.

[0086] As noted above, processes described herein are useful to electroplate metals other than copper, for example, gold, silver, platinum, nickel, tin, lead, ruthenium, rhodium, iridium, osmium, rhenium, and palladium. Metal ions useful in the catholyte can be provided from a solution of a metal salt. Exemplary metal salts include gluconates, cyanides, sulfamates, citrates, fluoroborates, pyrophosphates, sulfates, chlorides, sulfides, chlorites, sulfites, nitrates, nitrites, and methane sulfonates. Exemplary concentrations of metal salts in the catholyte used for plating applications range from about 0.03 to about 0.25M.

[0087] The ability to electroplate metal ions can be affected by chelating the metal ion with a complexing agent. In the context of the electroplating of copper, copper ions chelated with ethylene diamine complexing agent exhibit a higher deposition potential compared to copper ions that have not been chelated. Complexing agents useful for chelating and forming complexes with metal ions include chemical compounds having at least one part with the chemical structure $\text{COOR}_1\text{—COHR}_2\text{R}_3$ where R_1 is an organic group or hydrogen covalently bound to the carboxylate group (COO), R_2 is either hydrogen or an organic group, and R_3 is either hydrogen or an organic group. Specific examples of such type of complexing agents include citric acid and salts thereof, tartaric acid and salts thereof, diethyltartrate, diisopropyltartrate, and dimethyltartrate. Another type of useful complexing agent includes compounds that contain a nitrogen containing chelating group $\text{R—NR}_2\text{—R}_1$, wherein R is any alkyl group, aromatic group, or polymer chain and R_1 and R_2 are H, alkyl or aryl organic groups. Specific examples of these types of complexing agents include ethylene diamine, ethylene diamine tetraacetic acid and its salts, cyclam, porphrin, bipyridyl, pyrrolle, thiophene, and polyamines. In plating embodiments, suitable ratios between the concentration of

metal ions and concentrations of complexing agents in the catholyte can range from 1:25 to 25:1; for example, 1:10 to 10:1 or 1:5 to 5:1.

[0088] Useful pH adjustment agents include materials capable of adjusting the pH of the first processing fluid and the second processing fluid, for example, to above 7 to about 13, and more specifically, above about 9.0. When ethylene diamine or citric acid are used as a complexing agent for copper ions, a pH of about 9.5 is useful. When ethylene diamine tetraacetic acid is used as a complexing agent for copper ions, a pH of about 12.5 is suitable. Examples of suitable pH adjustment agents include alkaline agents such as potassium hydroxide, ammonium hydroxide, tetramethyl ammonium hydroxide, sodium hydroxide, and other alkaline metal hydroxides. A useful amount and concentration of pH adjustment agents will depend upon the level of pH adjustment desired and other factors, such as the volume of processing fluid and the other components in the processing fluid. Useful pH adjustment agents also include materials capable of adjusting the pH of the first and second processing fluid to below 7.

[0089] For acidic processing fluids (low pH, high conductivity, high acid), useful pH adjustment agents include materials capable of adjusting the pH of the first and second processing fluid to below 7. Useful complexing agents for acid processing fluids include pyrophosphate, citric acid, ethylene diamine, ethylene diamine tetraacetic acid, polyimines, and polyamines.

[0090] Useful buffers for both alkaline and acidic processing fluids include materials that maintain the pH relatively constant, preferably at a level that facilitates complex formation and desirable complexed species. Boric acid was described above as an example of a suitable buffer. Other useful buffers include sodium acetate/acetic acid and phosphates. Exemplary concentrations of buffer range from about 0.001 to about 0.5 M in the catholyte for plating applications. Exemplary buffer concentrations for the anolyte range from about 0.001 to about 1.0 M.

[0091] The catholyte can include other additives such as those that lower the resistivity of the fluid, e.g., ammonium sulfate; and those that increase the conformality of the deposit, e.g., ethylene glycol. For plating applications, exemplary concentrations of resistivity effecting agents in the catholyte range from about 0.01 to about 0.5 M. For conformality affecting agents concentrations ranging from about 0 to 1.0 M are exemplary.

[0092] The catholyte can also include other additives such as an additive or combination of additives that suppresses the growth of metal nuclei on itself while permitting metal deposition onto the treated barrier layers. Through the use of such additives or additive combinations, nucleation of deposit metal on barrier layers can be promoted over growth of the metal itself. By promoting the nucleation of the metal to be deposited on the barrier layer as opposed to the growth of metal nuclei itself, metal deposition that is conformal (i.e., uniformly lines that feature) and continuous at small dimensions, e.g., thicknesses can be promoted.

[0093] Useful cation permeable barriers are generally selective to positively charged ions, e.g., hydrogen ions and metal ions; therefore, hydrogen ions and metal ions may migrate through the useful cation permeable barriers.

[0094] Useful cation permeable barriers include nonporous barriers, such as semi-permeable cation exchange membranes. A semi-permeable cation exchange membrane allows

cations to pass but not non-cationic species, such as anions. The nonporous feature of the barrier inhibits fluid flow between first processing fluid **406** and second processing fluid **412** within reactor **400** in FIG. 1. Accordingly, an electric potential, a charge imbalance between the processing fluids, and/or differences in the concentrations of substances in the processing fluids can drive cations across a cation permeable barrier. In comparison to porous barriers, nonporous barriers are characterized by having little or no porosity or open space. In a normal electroplating reactor, nonporous barriers generally do not permit fluid flow when the pressure differential across the barrier is less than about 6 psi. Because the nonporous barriers are substantially free of open area, fluid is inhibited from passing through the nonporous barrier. Water, however, may be transported through the nonporous barrier via osmosis and/or electro-osmosis. Osmosis can occur when the molar concentration in the first and second processing fluids are substantially different. Electro-osmosis occurs as water is carried through the nonporous barrier with current-carrying ions in the form of a hydration sphere. When the first and second processing fluids have similar molar concentrations and no electrical current is passed through the processing fluids, fluid flow between the first and second processing fluids via the nonporous barrier is substantially prevented.

[0095] A nonporous barrier can be hydrophilic so that bubbles in the processing fluids do not cause portions of the barrier to dry, which reduces conductivity through the barrier. Examples of useful cation permeable barriers include commercially available cation permeable membranes. For example, Tokuyama Corporation manufactures and supplies various hydrocarbon membranes for electro dialysis and related applications under the trade name Neosepta™. Perfluorinated cation membranes are generally available from DuPont Co. as Nafion™ membranes N-117, N-450, or from Asahi Glass company (Japan) under the trade name Flemion™ as Fx-50, F738, and F893 model membranes. Asahi Glass Company also produces a wide range of polystyrene based ion-exchange membranes under the trade name Selemion™, which can be very effective for concentration/desalination of electrolytes and organic removal (cation membranes CMV, CMD, and CMT and anion membranes AMV, AMT, and AMD). There are also companies that manufacture similar ion-exchange membranes (Solvay (France), Sybron Chemical Inc. (USA), Ionics (USA), and FuMA-Tech (Germany), etc.). Bipolar membranes, such as models AQ-BA-06 and AQ-BA-04, for example, are commercially available from Aqualitics (USA) and Asahi Glass Company may also be useful.

[0096] In addition to the nonporous barriers described above, cation permeable barrier can also be a porous barrier. Porous barriers include substantial amounts of open area or pores that permit fluid to pass through the porous barrier. Both cationic materials and nonionic materials are capable of passing through a porous barrier; however, passage of certain materials may be limited or restricted if the materials are of a size that allows the porous barrier to inhibit their passage. While useful porous barriers may limit the chemical transport (via diffusion and/or convection) of some materials in the first processing fluid and the second processing fluid, they allow migration of cationic species (enhanced passage of current) during application of electric fields associated with electrolytic processing. In the context of electrolytic processing a useful porous barrier enables migration of cationic species

across the porous barrier while substantially limiting diffusion or mixing (i.e., transport across the barrier) of larger organic components and other non-cationic components between the anolyte and catholyte. Thus, porous barriers permit maintaining different chemical compositions for the anolyte and the catholyte. The porous barriers should be chemically compatible with the processing fluids over extended operational time periods. Examples of suitable porous barrier layers include porous glasses (e.g., glass frits made by sintering fine glass powder), porous ceramics (e.g., alumina and zirconia), silica aerogel, organic aerogels (e.g., resorcinol formaldehyde aerogel), and porous polymeric materials, such as expanded Teflon® (Gortex®). Suitable porous ceramics include grade P-6-C available from CoorsTek of Golden, Colo. An example of a porous barrier is a suitable porous plastic, such as Kynar™, a sintered polyethylene or polypropylene. Suitable materials can have a porosity (void fraction) of about 25%-85% by volume with average pore sizes ranging from about 0.5 to about 20 micrometers. Such porous plastic materials are available from Poretex Corporation of Fairburn, Ga. These porous plastics may be made from three separate layers of material that include a thin, small pore size material sandwiched between two thicker, larger pore-sized sheets. An example of a product useful for the middle layer having a small pore size is CelGard™ 2400, made by CelGard Corporation, a division of Hoechst, of Charlotte, N.C. The outer layers of the sandwich construction can be a material such as ultra-fine grade sintered polyethylene sheet, available from Poretex Corporation. Porous barrier materials allow fluid flow across themselves in response to the application of pressures normally encountered in an electrochemical treatment process, e.g., pressures normally ranging from about 6 psi and below.

[0097] Inert anodes useful in processes described herein are also referred to as non-consumable anodes and/or dimensionally stable anodes and are of the type that when an electric potential is applied between a cathode and an anode in contact with an electrolyte solution, that there is no dissolution of the chemical species of the inert anode. Exemplary materials for inert anodes include platinum, ruthenium, ruthenium oxide, iridium, and other noble metals.

[0098] Consumable anodes useful in processes described herein are of the type that when an electric potential is applied between a cathode and an anode in contact with an electrolyte solution, dissolution of the chemical species making up the anode occurs. Exemplary materials for consumable anodes will include those materials that are to be deposited onto the microfeature workpiece, for example, copper, tin, silver, lead, nickel, cobalt, zinc, and the like.

[0099] The temperature of the processing fluids can be chosen taking into consideration conventional factors such as complexing ability of the complexing agent, buffering capability of the buffer, metal ion concentration, volatile organics concentration, deposition potential of the complexed metal at the particular pH, solubility of the processing fluid constituents, stability of the processing fluids, desired deposit characteristics, and diffusion coefficients of the metal ions. Generally, temperatures ranging from about 20° C.-35° C. are suitable, although temperatures above or below this range may be useful.

[0100] As described above in the context of an electroplating process, oxidation of hydroxyl ions or water at the anode produces oxygen capable of oxidizing components in the catholyte. When a cation permeable barrier is absent, oxida-

tion of components in the electrolyte can also occur directly at the anode. Oxidation of components in an electrolyte is undesirable because it is believed that the oxidized components contribute to variability in the properties (e.g. resistivity) of the metal deposits. Through the use of cation permeable barrier, as described above, transfer of oxygen generated at the anode from the anolyte to the catholyte is minimized and/or prevented, and, thus, such oxygen is not available to oxidize components that are present in the catholyte. As discussed above, one way to address the problem of oxygen generated at the anode oxidizing components in the processing fluid is to frequently replace the processing fluid. Because of the time and cost associated with frequently replacing the processing fluid, the processes described herein provide an attractive alternative by allowing the processing fluids to be used in a large number of plating cycles without replacement. Use of the cation permeable barrier also isolates the anode from non-cationic components in the catholyte, e.g., complexing agent, that may otherwise be oxidized at the anode and adversely affect the ability of the catholyte to deposit features having acceptable properties such as resistivity properties that fall within acceptable ranges.

[0101] Another advantage of employing a cation permeable barrier in the processes described herein is that the barrier prevents bubbles from the oxygen or hydrogen gas evolved at the anode from transferring to the catholyte. Bubbles in the catholyte are undesirable because they can cause voids or holes in the deposited features.

[0102] In the foregoing descriptions, copper has been used as an example of a metal that can be used to enhance a seed layer or to form a metal feature directly onto a barrier layer. However, it should be understood that the basic principles of the processes described herein and their use for enhancement of an ultrathin metal layer prior to the bulk deposition of additional metal or the direct electroplating of a metal onto a barrier layer can be applied to other metals or alloys as well as deposition for other purposes. For example, gold is commonly used on for thin film head and III-V semiconductor applications. Gold ions can be electroplated using chloride or sulfite as the counter ion. As with copper, the gold and hydrogen ions would migrate across the cationic permeable barrier as described above in the context of copper. Potassium hydroxide could be used as the pH adjustment agent in a gold electroplating embodiment to counteract a drop in pH in the catholyte resulting from migration of hydrogen ions from the anolyte to the catholyte. If needed an agent to counteract the loss of hydrogen ions from the anolyte can be added to the anolyte. As with the copper example described above, in the gold embodiment using an inert anode, gold chloride or gold sulfite, in the form of sodium gold sulfite or potassium gold sulfite could be added to the catholyte to replenish the gold deposited.

[0103] As mentioned previously, processes described above are useful for depositing more than one metal ion onto a microfeature workpiece surface. For example, processes described above are useful for depositing multi-component solders such as tin-silver solders. Other types of multi-component metal systems that can be deposited using processes described above include tin-copper, tin-silver-copper, lead-tin, nickel-iron, and tin-copper-antimony. Unlike certain copper features that are formed on the surfaces of microfeature workpieces, solder features tend to be used in packaging applications and are thus large compared to copper microfeatures. Because of their larger size, e.g., 10-200 microns, sol-

der features are more susceptible to the presence of bubbles in processing fluids that can become entrapped and affect the quality of the solder deposits. A tin-silver solder system is an example of plating of a metal with multiple valence states. Generally, metals with multiple valence states can be plated from most of their stable states. Since the charge required to deposit any metal is directly proportional to the electrons required for the reduction, metals in their valence states closest to their neutral states consume less energy for reduction to metal. Unfortunately, most metals in their state closest to their neutral states are inherently unstable, and therefore production-worthy plating can be unfeasible. Through the use of processes for plating metal ions described above, plating solutions that include metals in this inherently unstable state can be applied in an effective process to deposit the desired metal. Through the use of the processes described above for depositing a metal, less oxidation of the inherently unstable metal species occurs, thus providing a more production-worthy process.

[0104] By way of illustration, most tin-silver plating solutions prefer Sn(II) as the species for tin plating. For such multi-component plating systems, control of tin and silver ions needs to be precise. Multi-component plating systems can use inert or consumable anodes. The use of consumable anodes could cause stability issues resulting from plating/ reacting of one of the metals with the anodes, and they also create issues relating to the ability to uniformly replenish metal. On the other hand, the use of inert anodes avoids the foregoing issues, but introduces a new issue associated with the production of oxygen through the oxidation of water or hydroxyl ions at the inert anode. Such oxygen not only may oxidize other components in the plating bath, it may also oxidize the desired species, e.g., Sn(II) to the more stable species, e.g., Sn(IV) ion, which is more difficult to plate onto a workpiece.

[0105] Referring to FIG. 6, a schematic illustration is provided for the operation of reactor 610 using a cation permeable barrier 624 and an inert anode 622 in combination with a first processing fluid 614 and a second processing fluid 620 suitable for depositing tin-silver solder. In the description that follows, processing fluid 614 in processing unit 612 is a catholyte containing metal ions M_1^+ and M_2^+ , e.g., Sn^{2+} and Ag^+ ions; counter ions X_1^- and X_2^- for the metal ions, e.g., methane sulfonate $CH_3SO_3^-$; and complexing agents CA_1 and CA_2 , e.g., proprietary organic additives, chelated with the metal ions, hydrogen ions and hydroxyl ions. As discussed above in the context of the electroplating of copper, the specific hydrogen ion concentration in catholyte 614 can be chosen taking into consideration conventional factors such as complexing ability of the complexing agent, buffering capability of the buffer, metal ion concentrations, volatile organics concentrations, alloy deposition potential of the complex at the particular pH, solubility of the catholyte constituents, stability of the catholyte, desired characteristics of the deposits, and diffusion coefficients of the metal ions.

[0106] The discussions above regarding the concentration of H^+ in the anolyte and catholyte, relative concentrations of the buffer in the anolyte and the catholyte, use of the pH adjustment agent, replenishment of the metal ions, cathodic reduction reactions, and anodic oxidation reactions in the context of the electroplating of copper are equally applicable to a tin-silver system. The particular operating conditions that are most desirable are related to the specific chemistry being used.

[0107] As with the copper plating process, an electric potential applied between cathode 616 and anode 622 results in tin ions and silver ions being reduced at cathode 616 and deposited thereon. The hydrogen ion (H^+) accumulates in the anolyte near a first surface 632 of cation permeable barrier 624. As with the copper system, at positively charged inert anode 622, water is converted to hydrogen ions (H^+) and oxygen. The resulting electrical charge gradient urges positively charged hydrogen ions (H^+) to move from first surface 632 of cation permeable barrier 624 to the second surface 634 of cation permeable barrier 624. The transfer of positively charged hydrogen ions from anolyte 620 to catholyte 614 during the plating cycle maintains the charge balance of reactor 610. As noted in FIG. 6, the concentration of hydrogen ion in anolyte 620 is higher than the concentration of hydrogen ion in catholyte 614. This concentration gradient also urges hydrogen ions to transfer from anolyte 620 to catholyte 614 through cation permeable barrier 624. Tin and silver ions that are deposited onto cathode 616 can be replenished by the addition of a solution of tin methane sulfonate and silver methane sulfonate to the catholyte. During the plating cycle, MSA ions that are introduced to catholyte 614 as a result of the addition of the tin MSA and silver MSA build up and must eventually be removed. Portions of the catholyte can be removed from processing unit 612 to address the buildup of MSA ions in the catholyte.

[0108] Alternatively, the tin and/or silver ions could be added to anolyte 620 under conditions wherein the hydrogen ion concentration in the catholyte 614 is greater than the hydrogen ion concentration of anolyte 620. Under these conditions, movement of hydrogen ions from anolyte 620 to catholyte 614 is inhibited by the hydrogen ion concentration gradient and the metal ions in the anolyte transfer to the catholyte and contribute to maintaining the charge balance of the reactor. Under these conditions, steps can be taken to mitigate any issues created by metal ions oxidizing in anolyte 620.

[0109] Referring to FIG. 7, in a different embodiment, electroplating of two metals, e.g., tin and silver, can also be achieved using a consumable anode 722. Referring to FIG. 7, the catholyte 714 in processing unit 712 is similar to the catholyte described with reference to FIG. 6. In the process depicted in FIG. 7, metal ion M_2^+ is introduced into processing unit 712 from source 700, metal ion M_1^+ is supplied to counter electrode unit 718 through oxidation of metal making up consumable anode 722. Metal ion M_1^+ in anolyte 716 moves across cation permeable barrier 720 into catholyte 714. Movement of metal ion M_1^+ helps to maintain the charge balance of reactor 730. In addition, movement of metal ion M_1^+ from anolyte 716 to catholyte 714 is also promoted by a metal ion M_1^+ concentration gradient between anolyte 716 and 714, i.e., metal ion M_1^+ concentration in anolyte 716 is greater than the metal ion M_1^+ concentration in catholyte 714. Metal ions M_1^+ and M_2^+ can be reduced at cathode 724 and deposited thereon as described above with reference to FIG. 6. In accordance with this embodiment, complexing agents (CA) are present in catholyte 714 where they can complex with metal ions M_1^+ and M_2^+ . Suitable pH adjustment agents and pH buffers may be present and/or added to the catholyte and anolyte. The charge balance within reactor 730 can be maintained through the transfer of positively charged metal ion M_1^+ in counter-electrode unit 718 across cation permeable membrane 720 into processing unit 712. In this system, movement of hydrogen ions from anolyte 716 to catholyte

714 in order to provide charge balance is inhibited (in favor of transfer of M_1^+) by providing a higher concentration of hydrogen ion in catholyte **714** than in anolyte **716**. In such a system, metal ion M_2^+ does not come into contact with anode **722** where it may undesirably deposit depending upon the deposition potentials of metal ion M_2^+ and metal ion M_1^+ . It is contemplated that cations in addition to metal ion M_1^+ could pass through cation permeable barrier **720** from anolyte **716** to catholyte **714**, for example by reversing the hydrogen ion concentration gradient described above. When the hydrogen ion concentration gradient is reversed, e.g., the hydrogen ion concentration of the anolyte is greater than the hydrogen ion concentration of the catholyte, hydrogen ions will more readily transfer from anolyte **716** to catholyte **714**. In addition, it is contemplated that other metal ions in addition to M_1^+ could be added to anolyte **716** and transfer from anolyte **716** to catholyte **714** through cation permeable barrier **720**.

[0110] Suitable reactors for depositing tin ions and silver ions includes one designated a Raptor™ by Semitool, Inc., of Kalispell, Mont., or a reactor of the type described in U.S. Patent Application Ser. No. 60/739,343, filed on Nov. 23, 2005, entitled Apparatus and Method for Agitating Fluids and the Processing of Microfeature Workpieces.

[0111] Metal can be depleted from a microfeature workpiece by reversing the bias of the electric field created between the microfeature workpiece and the working electrode. Referring to FIG. 10, a microfeature workpiece **516** is provided that carries a metal M, e.g., copper, on its surface. Microfeature workpiece **516** is contacted with a first processing fluid **514** in processing unit **512**. Processing fluid **514** includes metal ions M^+ , e.g., copper ions; a complexing agent CA, e.g., ethylene diamine tetraacetic acid; a metal salt MX, e.g., copper sulfate or copper phosphate; a complexed metal ion $M(CA)^+$; hydroxyl ions; a buffer, and a counter ion X^- , e.g., phosphate or sulfate ion. Processing unit **512** is separated from a counter electrode unit **518** by cation permeable membrane **524**. Counter electrode unit **518** includes counter electrode **522** and a second processing fluid **520**. In a deplating process, microfeature workpiece **516**, the working electrode, is an anode, and counter electrode **522** is the cathode. Processing unit **512** is also in fluid communication with a source **530** of complexing agent CA and a source **532** of hydrogen ions. Counter electrode unit **518** is in fluid communication with a source **550** of pH adjustment agent. Through the application of an electric potential between anode **516** and cathode **522**, hydrogen ions are reduced at the cathode **522** to produce hydrogen gas. Metal on the surface of microfeature workpiece **516** is oxidized resulting in metal ions being removed from the surface of the microfeature workpiece. The charge balance within reactor **540** is maintained through the transfer of hydrogen ions from catholyte **520** to anolyte **514** through cation permeable membrane **524**.

[0112] Catholyte **520** in counter electrode unit **518** includes hydrogen ions, hydroxyl ions, buffer, and counter ion X^- . The pH adjustment agent that is added to counter electrode unit **518** can be both a source of counter ion X^- as well as hydrogen ions (H^+). Over time, metal ion M^+ builds up in concentration in anolyte **514**. Accordingly, periodic purging and replenishing of anolyte **514** may be necessary. Charge balance within reactor **540** is maintained by transfer of hydrogen ions from anolyte **514** to catholyte **520**. To further promote movement of hydrogen ions from anolyte **514** through cation permeable barrier **524** to catholyte **520**, a hydrogen ion concentration gradient can be established between anolyte **514**

and catholyte **520**. In other words, the concentration of hydrogen ions in anolyte **514** can be greater than the concentration of hydrogen ions in catholyte **520**. While it is possible for metal ion M^+ to also transfer from anolyte **514** to catholyte **520**, it is preferred that the charge balance be maintained primarily through movement of hydrogen ions as opposed to metal ions. If it is desired to have the metal ion serve as the major charge carrier to maintain charge balance within reactor **540**, movement of hydrogen ions across cation permeable barrier **524** can be inhibited by reversing the hydrogen ion concentration, i.e., hydrogen ion concentration of the catholyte is greater than the hydrogen ion concentration of the anolyte.

[0113] Referring to FIG. 8, a more detailed schematic illustration of one design of a reactor **8** for directly electroplating metal onto barrier layers or otherwise depositing materials onto workpieces using a cation permeable barrier is illustrated. Reactor **824** includes a vessel **802**, a processing chamber **810** configured to direct a flow of first processing fluid to a processing zone **812**, and an anode chamber **820** configured to contain a second processing fluid separate from the first processing fluid. A cation permeable barrier **830** separates the first processing fluid in the processing unit **810** from the second processing fluid in the anode chamber **820**. Reactor **820** further includes a workpiece holder **840** having a plurality of electrical contacts **842** for applying an electric potential to a workpiece **844** mounted to workpiece holder **840**. Workpiece holder **840** can be a movable head configured to position workpiece **844** in processing zone **812** of processing unit **810**, and workpiece holder **840** can be configured to rotate workpiece **844** in processing zone **812**. Suitable workpiece holders are described in U.S. Pat. Nos. 6,080,291; 6,527,925; 6,773,560, and U.S. patent application Ser. No. 10/497,460; all of which are incorporated herein by reference.

[0114] Reactor **824** further includes a support member **850** in the processing chamber **810** and a counter electrode **860** in the anode chamber **820**. Support member **850** spaces the cation permeable barrier **830** apart from workpiece processing zone **812** by a controlled distance. This feature provides better control of the electric field at processing zone **812** because the distance between the cation permeable barrier **830** and workpiece processing zone **812** affects the field strength at processing zone **812**. Support member **850** generally contacts first surface **832** of cation permeable barrier **830** such that the distance between first surface **832** and processing zone **812** is substantially the same across processing chamber **810**. Another feature of support member **850** is that it also shapes cation permeable barrier **830** so that bubbles do not collect along a second side **834** of cation permeable barrier **830**.

[0115] Support member **850** is configured to direct flow F_1 of a first processing fluid laterally across first surface **832** of cation permeable barrier **830** and vertically to processing zone **812**. Support member **850** accordingly controls the flow F_1 of the first processing fluid in processing chamber **810** to provide the desired mass transfer characteristics in processing zone **812**. Support member **850** also shapes the electric field in processing chamber **810**.

[0116] Counter electrode **860** is spaced apart from second surface **834** of cation permeable barrier **830** such that a flow F_2 of the second processing fluid moves regularly outward across second surface **834** of cation permeable barrier **830** at a relatively high velocity. Flow F_2 of the second processing fluid sweeps oxygen bubbles and/or particles from the cation

permeable barrier **830**. Reactor **824** further includes flow restrictor **870** around counter electrode **860**. Flow restrictor **870** is a porous material that creates a back pressure in anode chamber **820** to provide a uniform flow between counter electrode **860** and second surface **834** of the cation permeable barrier **830**. As a result, the electric field can be consistently maintained because flow restrictor **870** mitigates velocity gradients in the second processing fluid where bubbles and/or particles can collect. The configuration of counter electrode **860** and flow restrictor **870** also maintains a pressure in the anode chamber **820** during plating that presses the cation permeable barrier **830** against support member **850** to impart the desired contour to cation permeable barrier **830**. Reactor **824** operates by positioning workpiece **844** in processing zone **812**, directing flow F_1 of the first processing fluid through processing chamber **810**, and directing the flow F_2 of the second processing fluid through anode chamber **820**. As the first and second processing fluids flow through reactor **824**, an electric potential is applied to workpiece **844** via electrical contacts **842** and counter electrode **860** to establish an electric field in processing chamber **810** and anode chamber **820**.

[0117] Another useful reactor for depositing metals using processes described herein is described in U.S. Patent Application No. 2005/0087439, which is expressly incorporated herein by reference.

[0118] One or more of the reactors for electrolytically treating a microfeature workpiece or systems including such reactors may be integrated into a processing tool that is capable of executing a plurality of methods on a workpiece. One such processing tool is an electroplating apparatus available from Semitool, Inc., of Kalispell, Mont. Referring to FIG. 9, such a processing tool may include a plurality of processing stations **910**, one or more of which may be designed to carry out an electrolytic processing of a microfeature workpiece as described above. Other suitable processing stations include one or more rinsing/drying stations and other stations for carrying out wet chemical processing. The tool also includes a robotic member **920** that is carried on a central track **925** for delivering workpieces from an input/output location to the various processing stations.

[0119] Processes are further described for depositing more than one metal ion onto a microfeature workpiece surface. For example, the processes may be used for depositing multi-component solders. Although exemplary tin-silver solder plating processes using cation permeable barriers are described above, additional metals and processing conditions are described below solder plating. Other non-limiting examples of multi-component solders may include tin-silver-copper, tin-bismuth, tin-indium, tin-copper, tin-bismuth-indium, and tin-bismuth-zirconium.

[0120] The processes described herein may be used for electrochemical deposition of two or more metals ions. In one embodiment of the present disclosure, the solder deposited includes at least first and second metal ions. The first metal ion may be selected from the group consisting of copper ion, lead ion, gold ion, tin ion, silver ion, bismuth ion, indium ion, platinum ion, ruthenium ion, rhodium ion, iridium ion, osmium ion, rhenium ion, palladium ion, and nickel ion, etc. Likewise, the second metal ion may be selected from the group consisting of copper ion, lead ion, tin ion, silver ion, bismuth ion, indium ion, platinum ion, ruthenium ion, rhodium ion, iridium ion, osmium ion, rhenium ion, palladium ion, nickel ion, etc.

[0121] In ternary alloys, the solder deposit may include a third metal ion also selected from the group consisting of copper ion, lead ion, gold ion, tin ion, silver ion, bismuth ion, indium ion, platinum ion, ruthenium ion, rhodium ion, iridium ion, osmium ion, rhenium ion, palladium ion, nickel ion, etc.

[0122] In accordance with one embodiment of the present disclosure, a process for electrolytically processing a microfeature workpiece as the working electrode in a first processing fluid and a counter electrode in a second processing fluid generally includes contacting a surface of the microfeature workpiece with the first processing fluid, the first processing fluid including a first metal cation, and contacting the counter electrode with a second processing fluid, the second processing fluid including a second metal cation. The process further includes allowing the second metal cation to move from the second processing fluid to the first processing fluid, but substantially preventing movement of the first metal cation from the first processing fluid to the second processing fluid. The process further includes electrolytically depositing the first and second metal cations onto the surface of the microfeature workpiece.

[0123] In the exemplary tin-silver solder deposition described above, the first processing fluid is a catholyte and the second processing fluid is an anolyte. The cathode is the workpiece, and the anode is either a consumable or inert anode, as discussed in greater detail below.

[0124] Preventing movement of the first metal cation from the first processing fluid to the second processing fluid may include the use of a cation permeable barrier in combination with a suitable charge balance to prevent movement of the first metal cation from the first processing fluid to the second processing fluid, but to allow movement of the second metal cation from the second processing fluid to the first processing fluid. Useful cation permeable barriers include nonporous barriers, such as semi-permeable cation exchange membranes. Suitable cation permeable membranes are discussed above.

[0125] As discussed above with reference to FIG. 7, electroplating of two metals, e.g., tin and silver, can be achieved using a consumable anode **722**. (See FIG. 6 and related discussion above regarding a process using an inert anode.) Referring to FIG. 7, the catholyte **714** in processing unit **712** is similar to the catholyte described with reference to FIG. 6. In the process depicted in FIG. 7, metal ion M_2^+ is introduced into processing unit **712** from source **700**, metal ion M_1^+ is supplied to counter electrode unit **718** through oxidation of metal making up consumable anode **722**. Metal ion M_1^+ in anolyte **716** moves across cation permeable barrier **720** into catholyte **714**. Movement of metal ion M_1^+ helps to maintain the charge balance of reactor **730**. In addition, movement of metal ion M_1^+ from anolyte **716** to catholyte **714** may also be promoted by a metal ion M_1^+ concentration gradient between anolyte **716** and catholyte **714**, i.e., metal ion M_1^+ concentration in anolyte **716** may be greater than the metal ion M_1^+ concentration in catholyte **714**. However, such metal concentration gradient may not be required between the anolyte and the catholyte if the major driving force of metal ion M_1^+ is the current and not the concentration gradient. In that regard, the metal ion M_1^+ concentration in anolyte **716** may be less than the metal ion M_1^+ concentration in catholyte **714**.

[0126] Metal ions M_1^+ and M_2^+ can be reduced at cathode **724** and deposited thereon as described above with reference to FIG. 6. In accordance with this embodiment, complexing

agents (CA) are present in catholyte 714 where they can complex with metal ions M_1^+ and M_2^+ . Suitable pH adjustment agents and pH buffers may be present and/or added to the catholyte and anolyte. The charge balance within reactor 730 can be maintained through the transfer of positively charged metal ion M_1^+ in counter-electrode unit 718 across cation permeable membrane 720 into processing unit 712. In this system, movement of hydrogen ions from anolyte 716 to catholyte 714 in order to provide charge balance is inhibited (in favor of transfer of M_1^+) by providing a higher concentration of hydrogen ion in catholyte 714 than in anolyte 716. In such a system, metal ion M_2^+ does not come into contact with anode 722 where it may undesirably deposit depending upon the deposition potentials of metal ion M_2^+ and metal ion M_1^+

[0127] When the current is running, the first metal cation (such as silver ion) does not cross the cation permeable barrier from the first processing fluid into the second processing fluid because of the charge balance. However, when the current is not running the first and second processing fluids may need to be separated from each other to prevent migration of the first metal cation from the first processing fluid to the second processing fluid and to prevent the back draft of protons (H^+) ions from the catholyte to the anolyte. Such separation may be achieved by reducing the anolyte volume in the anolyte chamber such that the upper surface of the anolyte is no longer in intimate contact with the membrane. In that regard, when the current is not running in the system, a valve may be opened to allow anolyte fluid to drain from the anolyte chamber.

[0128] By preventing the movement of the first metal cation to the second processing fluid, the anode ideally does not come into contact with the ions of the more noble metal. In a non-limiting exemplary silver/tin alloy system using a consumable tin anode, if silver ions were to contact the tin anode, they would deposit on the tin anode and continuously be extracted from solution. At the same time, the tin would become corroded and tin ions would enter the electrolyte by a displacement reaction. Once silver metal deposits on a tin anode, it cannot be easily removed electrolytically. If tin metal is available in the anode and exposed to the solution, the applied potential will not be sufficiently anodic to remove the silver.

[0129] To avoid this displacement reaction in the exemplary silver/tin alloy system, it is important that the tin anode avoid contact with the silver ions in the bath. Therefore, movement of the first metal cation from the first processing fluid to the second processing fluid is substantially prevented. In one embodiment of the present disclosure, a cation selective membrane is used to separate the catholyte and anolyte. The membrane allows tin ions to pass from the anolyte to the catholyte to replenish consumed tin in the deposition chemistry, but the membrane substantially prevents silver ions from passing from the catholyte to the anolyte.

[0130] For tin ions to pass through the membrane from the anolyte to the catholyte, the tin ions must be the primary charge carrier. Because of the level of acidity in an acid-based chemistry system, protons (H^+) tend to be the primary charge carrier instead of tin ions, except in the case in which there is a higher pH in the anolyte than in the catholyte (thereby starving the anolyte of protons). The target pH in the catholyte for exemplary tin/silver alloy deposition is generally less than 1.0, or less than 0.5. Such a target pH in the catholyte improves the conductivity of the chemistry and the solubility for metal ions. And, the pH of the anolyte is greater than the pH of the catholyte to create a pH gradient such that the

second metal cations (e.g., tin ions) are the primary charge carrier through the membrane instead of protons.

[0131] Further complicating the chemistry, tin solubility in a methane sulfonic acid (MSA) solution decreases dramatically as pH approaches 2. Therefore, in order to have a higher pH in the anolyte than in the catholyte, a suitable anolyte solution is maintained at a pH higher than 1 but less than 2. However, with chemistry developments, a pH of greater than 2 may be achieved. In accordance with embodiments of the present disclosure, the inventors have found that a ratio of at least 30-40 to 1 of metal ions to protons in the anolyte improves the mass transfer of metal ions across the membrane. Referring to FIG. 11, which shows the relationship between the molar concentration of tin ions in the anolyte and the pH of the anolyte, the preferred ratio may correspond to a pH of about 1.8 to 2.0. In another embodiment, a ratio of at least 100 to 1 of metal ions to protons in the anolyte improves the mass transfer of metal ions across the membrane. Referring to FIG. 11, this ratio may correspond to a pH of about 2.2.

[0132] In accordance with embodiments of the present disclosure, additives in the chemistry may allow the pH of the anolyte may get close to 2.0 or even exceed 2.0. Suitable additives may include stabilizing agents, chelating agents, metal complexing agents, and/or buffers to help the ions in the anolyte stay in solution, even though the pH approaches or exceeds 2.0.

[0133] In one embodiment of the present disclosure, the target pH of the anolyte is in the range of greater than 1.0 to less than 2.0. In another embodiment, the target pH of the anolyte is in the range of about 1.2 to about 1.8. In another embodiment, the target pH of the anolyte is greater than about 2.0. In another embodiment, the target pH of the anolyte is in the range of about 2.0 to about 3.0. In another embodiment, the target pH of the anolyte is in the range of about 1.0 to about 3.0.

[0134] In another embodiment, the target pH of the anolyte is in the range of about 1.5 to about 2.2. In this pH range the ratio of $Sn(2+)$ ions to H^+ ions (proton) in solution is about 40 to about 100 to 1. In this pH range and with this ratio of tin to proton ions, an acceptable range for membrane efficiency may be achieved, as discussed in greater detail below.

[0135] For complementary catholyte chemistry, in one embodiment of the present disclosure, the target pH of the catholyte is less than 1.0, and also less than the pH of the anolyte. In a different alloy plating system, as described in U.S. Patent Publication No. US2012/0138471, to Mayer et al. (hereinafter "Mayer"), a pH gradient is not required because of hardware differences in the system. In Mayer, fluid from the anolyte is pumped into the catholyte (see, e.g., conduit 259 in FIGS. 2B, 3, and 4 of Mayer). Therefore, the movement of tin ions in an exemplary tin/silver system is primary through conduit 259, and not across a cation permeable membrane. Rather, the purpose of the membrane in Mayer is to prevent the movement of silver ions into the anolyte to keep the silver ions from depositing on the tin anode.

[0136] In the system taught by Mayer, the tin ion concentration would be higher in the anolyte, and then the anolyte would be used to dose the catholyte. Because other chemistry components move when the anolyte doses the catholyte (for example, excess water, protons, and chemistry additives) and accumulate in the catholyte, the catholyte in the Mayer system will likely need to be occasionally bled and rebalanced to return to its desired parameters. Although a bleed and feed

process is effective for chemistry control, it wastes material and significantly increases the operating costs for the system, particularly in cost-sensitive wafer level packaging applications.

[0137] Because the dominant movement of tin ions in the Mayer system is through conduit 259 and not across the cation permeable membrane, a pH gradient between the anolyte and the catholyte is not needed for tin ion transport across the membrane. Therefore, the anolyte can be maintained at a pH similar to the pH of the catholyte.

[0138] Although Mayer discusses a pH range for the anolyte to be less than 2.0, the examples provided in Mayer have an anolyte pH of much lower than 1.0, in the range of about 0 to about 0.5. In that regard, the exemplary anolyte chemistries in Mayer include, respectively, 40-140, 80, 50, 180-350 g/l of methanesulfonate acid (MSA). As provided in a graphical representation of anolyte pH data in FIG. 13, the amount of MSA in the anolyte chemistry significantly affects pH. Even 1.0 g/l of MSA will bring the pH of the anolyte well below 2.0. It is estimated that with the amount of MSA

about 5.0 g/L. Because the silver ion is dosed into the catholyte and the system substantially prevents movement of the silver metal cation from the catholyte to the anolyte, there is little to no silver ion concentration expected in the anolyte.

[0144] In accordance with other embodiments of the present disclosure, other exemplary solders may include copper-silver-tin, tin-gold, and tin-bismuth. Near eutectic ranges for an exemplary solders are about $\pm 10\%$ of the eutectic ranges. However, it should be appreciated that the properties of the solders change as the compositions change. For example, desirable solder properties may include desirable grain structure, uniform melting point, malleability, and less brittleness.

EXAMPLES

[0145] Exemplary catholyte and anolyte bath components are provided in the table below. The acid may be MSA. Notably, the acid content in the anolyte is in the range of 0.5 to 2.5 g/l to achieve a suitable pH range for the anolyte according to the graphical representation of data in FIG. 13.

Bath	Catholyte#1 (MMCTS507)	Catholyte#2 (MMCTS304)	Catholyte#3 (DowTS4000)	Catholyte#4 (DowTS6000)	Anolyte#1
Sn	75-95 g/l	70-85 g/l	50-75 g/l	50 g/l	30-75 g/l
Ag	1-2 g/l	2.3-2.6 g/l	0.3-1 g/l	.3-.6 g/l	0 g/l
Acid	80-350 g/l	100-350 g/l	225 g/l	100-300 g/l	0.5-2.5 g/l

provided in the examples in Mayer, the pH of the anolyte in Mayer will be in the range of 0 to 0.5.

[0139] In contrast, in accordance with embodiments of the present disclosure, tin ions are the dominant ion of mass transfer across the cationic membrane, thereby substantially reducing the movement of other chemistry components from the anolyte to the catholyte, such as water, protons, and chemistry additives.

[0140] In accordance with embodiments of the present disclosure, a suitable cationic membrane is chemically compatible with MSA and efficient at transferring tin ions. In one embodiment, the membrane has high current carrying capability. For example, the tin-silver deposition process often operates in the range of 30-50 Amps to achieve high plating rates. Achieving a stable anolyte and catholyte generally means that for every tin atom plated on the wafer, one tin ion from the anolyte has to cross the membrane into the catholyte.

[0141] In the exemplary tin-silver solder deposition in accordance with embodiments of the present disclosure, the solder may be a near eutectic solder. A eutectic solder will solidify at a lower temperature compared to any other composition made up of the same ingredients. Eutectic tin-silver solder has 3.5% silver content. Near eutectic may be in the range of about 0.1% to about 5% silver content, about 0.5% to 5% silver content, about 1% to about 3% silver, or about 0.8% to about 5% silver content.

[0142] To achieve near eutectic tin-silver solder deposition, the composition of the catholyte may include a tin ion concentration in a range of about 40 to about 80 g/L, about 40 to about 120 g/L, or about 40 to about 150 g/L. As described in greater detail below, if the anode is a consumable tin anode, the concentration of tin ions in the anolyte is substantially similar to the concentration in the catholyte.

[0143] Likewise, the composition of the catholyte may include a silver ion concentration in a range of about 0.1 to

[0146] In addition to multi-component solders having metals that are deposited using an electrochemical deposition process, the multi-component solder may also include other co-deposited metals. Exemplary co-deposited metals may include small amounts of metals that are too electronegative to be deposited using ECD technology, for example, in the range of about 1 to about 100 ppm, or in the range of about 0.1% to about 20% by weight of deposit. An non-limiting examples, titanium and tantalum may be suitable co-deposited metals. Other non-limiting examples include vanadium, chromium, zirconium, niobium, molybdenum, hafnium, and tungsten. Although the metals cannot be deposited using ECD technology, if present in the catholyte chemistry, they can be found in the deposit as a result of physical deposition effects. To achieve a co-deposition composition of about 1 to about 100 ppm, the co-deposited metal may be present in the catholyte in a range of about 0.1 to about 15 g/L.

[0147] As discussed above, the anode may be a consumable anode for providing a source of metal ions into the anolyte. There are several advantages to using a consumable anode. For example, the cost of a tin concentrate solution is at a much higher cost than a tin consumable anode. Moreover, a consumable anode is a continuous, stable, self-controlling source of metal ions. In that regard, the concentration of metal ions in the anolyte is controlled in that for every ion deposited, one ion is consumed, one ion crosses membrane, and one ion is dissolved in solution. Through bath analysis (primarily tin and acid concentration), ion transport across the membrane against ion loss (plating) in the catholyte and ion generation in the anolyte can be tracked using Faraday's Law.

[0148] Experimental results from an exemplary tin/silver deposition system with a consumable tin anode are provided in FIGS. 12A and 12B. As can be seen in FIG. 12A, as anolyte pH approaches approximately 0.8 in an exemplary tin/silver deposition system (moving from left to right on the graph),

the tin concentrations in the catholyte and anolyte start to diverge from the expected concentrations. Also, as the pH continues to rise from 0.8 and approaches 1, the tin concentration in the catholyte starts to increase. Both observations indicate that if the pH is high enough, the tin ions become the primary charge carrier and start to pass thru the membrane from the anolyte to catholyte.

[0149] As can be seen in FIG. 12B, which is a graphical representation of the relationship between pH and tin concentration in the catholyte and the anolyte, if the anolyte pH in an exemplary tin/silver deposition system is maintained at a pH above 1, tin concentration in the catholyte can be maintained at close to target concentration. This observation indicates that consumed tin in the catholyte is replenished by tin ions pass thru the membrane from the anolyte.

[0150] In contrast to a consumable anode, dosing metal ions into the system has drawbacks. For example, when dosing metal ions into the anolyte or the catholyte, process control is retroactive, thereby resulting in a sawtooth concentration profile. Moreover, a metal ion concentrate may include other components to keep the metal ions in solution. As tin ions are consumed, these other components accumulate, affecting both bath stability and bath lifetime.

[0151] As described above, another advantage of employing a cation permeable barrier in the processes described herein is that the barrier prevents bubbles from the oxygen or hydrogen gas evolved at the anode from transferring to the catholyte. Bubbles in the catholyte are undesirable because they can cause voids or holes in the deposited features.

[0152] In an ideal system using a consumable anode, the charge balance is such that for each metal ion deposited, one ion crosses the membrane from the anolyte to the catholyte, and likewise, one ion is consumed from the consumable anode. However, it should be appreciated that an ideal system cannot always be achieved. For example, protons may move across the membrane in lieu of metal ions. Although the pH gradient between the anolyte and the catholyte is designed to such that metal ions (such as tin ions) dominate mass transfer, protons are more mobile, smaller, and move more easily than metal ions. Because of their mobility, any proton in the near vicinity of the membrane may carry current across the membrane.

[0153] In one embodiment of the present disclosure, 85% efficiency may be achieved. In another embodiment of the present disclosure, 90% efficiency may be achieved. In another embodiment of the present disclosure, 95% efficiency may be achieved.

[0154] Although the consumable anode may be a source of metal ions, it may not be the only source of metal ions. In that regard, in addition to the presence of metal ions from a consumable anode, an additional source of metal ions may be dosed in the catholyte. In one embodiment of the present disclosure, the primary source of metal ions comes from the consumable anode. In one embodiment of the present disclosure, the primary source of metal ions comes from dosing in the catholyte.

[0155] Moreover, when the system is starting up, there may be a need to chemically dose the system with a source of metal ions.

[0156] In accordance with another embodiment of the present disclosure, the primary source of metal ions may be dosing in the anolyte. In that regard, the process may include either a consumable anode or an inert anode.

[0157] Tin oxidation from Sn(II) to Sn(IV) is a common problem in a chemistry containing tin ions, resulting in a reduction in tin ions in the chemistry for plating. Tin oxidation can be mitigated by including antioxidants in the chemistry. Therefore, in accordance with another embodiment of the present disclosure, the system includes a method for mitigating oxidation. Antioxidants may be chemical antioxidants in solution that are sacrificial oxidants to use up any oxygen in the system before it oxidizes tin. Other antioxidants causing antioxidant effects in the system may include a degassing unit to remove oxygen in the catholyte and/or the anolyte, or may include nitrogen injection bubbling into the catholyte and/or the anolyte. The catholyte may be more prone to oxidation effects than the anolyte because the catholyte chamber may be open to the atmosphere allowing more oxygen to dissolve in solution.

[0158] While a preferred embodiment of the invention has been illustrated and described, it will be appreciated that various changes can be made therein without departing from the spirit and scope of the disclosure.

1. A process for electrolytically processing a microfeature workpiece as the working electrode in a first processing fluid and a counter electrode in a second processing fluid, the method comprising:

- (a) contacting a surface of the microfeature workpiece with the first processing fluid, the first processing fluid including at least a first metal cation;
- (b) contacting the counter electrode with a second processing fluid, the second processing fluid including a second metal cation;
- (c) allowing the second metal cation to move from the second processing fluid to the first processing fluid, but substantially preventing movement of the first metal cation from the first processing fluid to the second processing fluid by providing a cation permeable barrier between the first processing fluid and the second processing fluid, wherein the primary mass transport of the second metal cation from the second processing fluid to the first processing fluid is across the cation permeable barrier; and
- (d) electrolytically depositing the first and second metal cations onto the surface of the microfeature workpiece.

2. The process of claim 1, wherein the cation permeable barrier is a cation exchange membrane.

3. The process of claim 1, further comprising producing an electrochemical reaction at the counter electrode to produce the second metal cation.

4. The process of claim 1, wherein the working electrode is a cathode, and the counter electrode is an anode.

5. The process of claim 1, wherein the first processing fluid is dosed with the first metal cation.

6. The process of claim 1, wherein the counter electrode is a consumable electrode.

7. The process of claim 1, wherein either or both of the first and second processing fluids is dosed with the second metal cation.

8. The process of claim 7, wherein dosing in either or both of the first and second processing fluids with the second metal cation is not the major source of the second metal cation in the first processing fluid.

9. The process of claim 1, wherein the first metal cation concentration in the first processing fluid is in the range of about 0.1 g/L to about 5.0 g/L.

10. The process of claim 1, wherein the second metal cation concentration in the first processing fluid is selected from the group consisting of in the range of about 40 to about 80 g/L, about 40 to about 120 g/L, and about 40 to about 150 g/L.

11. The process of claim 1, wherein the pH of the second processing fluid is higher than the pH of the first processing fluid.

12. The process of claim 1, wherein the pH of the second processing fluid is selected from the group consisting of about 1.0 to about 2.0, about 1.2 to about 1.8, about 1.5 to about 2.2, greater than about 2.0, about 1.0 to about 3.0, and about 2.0 to about 3.0.

13. The process of claim 12, wherein the pH of the first processing fluid is selected from the group consisting of less than or equal to 1.0, less than or equal to 0.5, and in the range of 0 to 1.0.

14. The process of claim 1, wherein the first metal cation is selected from the group consisting of copper ion, lead ion, gold ion, tin ion, silver ion, bismuth ion, indium ion, platinum ion, ruthenium ion, rhodium ion, iridium ion, osmium ion, rhenium ion, palladium ion, and nickel ion.

15. The process of claim 1, wherein the second metal cation is selected from the group consisting of copper ion, lead ion, tin ion, bismuth ion, indium ion, silver ion, platinum ion, ruthenium ion, rhodium ion, iridium ion, osmium ion, rhenium ion, palladium ion, and nickel ion.

16. The process of claim 1, further comprising a third metal cation selected from the group consisting of copper ion, lead ion, gold ion, tin ion, silver ion, bismuth ion, indium ion, platinum ion, ruthenium ion, rhodium ion, iridium ion, osmium ion, rhenium ion, palladium ion, nickel ion.

17. (canceled)

18. The process of claim 1, wherein at least one of the first processing fluid and the second processing fluid includes an antioxidant.

19. (canceled)

20. The process of claim 1, where the second processing fluid is not dosed into the first processing fluid.

21. A process for electrolytically processing a microfeature workpiece as the working electrode with a first processing fluid and a counter electrode, comprising:

- (a) contacting a surface of the microfeature workpiece with the first processing fluid, the first processing fluid comprising first processing fluid species including at least a first metal cation;
- (b) contacting the counter electrode with a second processing fluid;
- (c) producing an electrochemical reaction at the counter electrode to produce a second metal cation in the second processing fluid;
- (d) providing a cation exchange membrane to allow the second metal cation to move from the second processing fluid to the first processing fluid, but to substantially prevent movement of the first metal cation from the first processing fluid to the second processing fluid when electrolytically processing the microfeature workpiece; and
- (e) separating the second processing fluid from the membrane when not electrolytically processing the microfeature workpiece.

22. A process for electrolytically processing a microfeature workpiece as the cathode with a first processing fluid and an anode, comprising:

- (a) contacting a surface of the microfeature workpiece with the first processing fluid, the first processing fluid comprising first processing fluid species including at least a first metal cation;
- (b) contacting the anode with a second processing fluid;
- (c) consuming the anode to produce a second metal cation in the second processing fluid;
- (d) providing a cation exchange membrane to allow the second metal cation to move from the second processing fluid to the first processing fluid, but to substantially prevent movement of the first metal cation from the first processing fluid to the second processing fluid, wherein the second processing fluid is not dosed in the first processing fluid; and
- (e) electrolytically depositing the first and second metal cations onto the surface of the microfeature workpiece.

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