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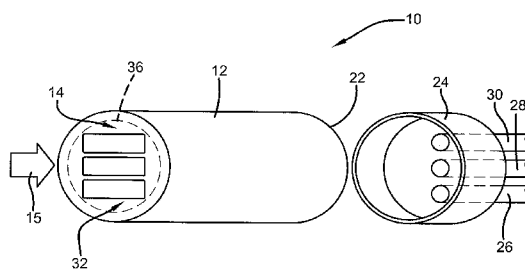


FIG. 1

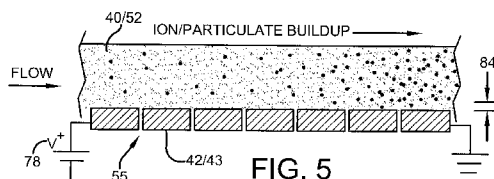


FIG. 5

(57) Abstract: A tunable membrane configuration (10) for a filtration or selective fluidic isolation and recovery device includes a housing (12) having an inlet at one end and an outlet at an opposite end with an opening extending from the inlet to the outlet. An internal support structure is maintained in the opening, and layered filtration media comprising graphene membranes (42/43) is carried by the internal support structure, the media separating feedwater received at the inlet into at least three separate output flows (26,28,30). Concentration polarisation (84) and pore size (55) can be controlled via an electrical charge control (78).

TUNABLE LAYERED GRAPHENE MEMBRANE CONFIGURATION FOR FILTRATION AND SELECTIVE  
ISOLATION AND RECOVERY DEVICES

5

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority of United States Provisional Application Serial No. 61/617,264 filed March 29, 2012, which is incorporated herein by reference.

TECHNICAL FIELD

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Generally, the present invention relates to a membrane configuration design for filtration and selective fluidic isolation and recovery devices. Specifically, the present invention relates to a layered membrane configuration for a filtration or selective fluidic isolation and recovery device. More particularly, the present invention is directed to a layered configuration of materials that include at least one high flux, high selectivity

15 membrane. The layers may be arranged in a planar, spiral wound or other alternate multiple pass configuration in dead end flow or cross flow.

BACKGROUND ART

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Currently, nearly half of the online capacity of desalinated water is achieved through a reverse osmosis filtering process. Reverse osmosis market share is growing but current reverse osmosis technology remains capital and energy intensive, with limitations in product design and performance based upon current polymer filtration membranes. The current industry standard for polymer filtration is an eight inch diameter by forty inch length spiral wound membrane with 400 to 440 square feet of active membrane area.

25 Such devices are limited in permeability which in turn limits output water per unit area, or flux, and requires increased membrane area and operating pressures. These high membrane area requirements and operating pressures are a result of membrane resistance (that is, permeability) as well as concentration polarization, scaling, fouling, and the like. As such, these filtration devices require frequent cleaning and ultimately replacement.

30 The limitations in relation to the flux and associated membrane area requirements result in significant capital cost. The need for high operating pressure devices increase the energy required to operate the filtration device and which further results in degradation of the membrane due to fouling and compaction which also adds to the operating cost.

35

Current filtration devices for reverse osmosis utilize an eight inch diameter by forty inch length spiral wound design. Within the filtration media there are twenty to thirty-four membrane leafs which provide for an active membrane area for maximum

filtration output. Although improvements have been made in the filtration media, these are only incremental improvements and do not address the issues raised in regard to limited flux throughput or the requirement for high operating pressures.

5 The reverse osmosis approach to filtering and/or desalination is to employ active filtering layers utilizing polyimide components. Such technology utilizes solution diffusion so as to separate the feed material into a concentrate and permeate. In the reverse osmosis technology, the membranes are susceptible to fouling, scaling and compaction. These materials also have limited chemical and biological resistance with limited methods of cleaning, which in turn relates to the need for frequent replacement of  
10 the filtration devices.

To protect the membrane materials, robust chemical conditioning and pretreatment is needed as a front end stage prior to desalination. Pretreatment is capital intensive and requires plant space, equipment, energy, and chemicals. Current pretreatment methods include conventional filtration and membrane filtration. Conventional filtration types  
15 include cartridge filtration and media filtration such as flocculation, sedimentation, dissolved air flotation, diatomaceous earth, granular media, pressure filters and gravity filters. Membrane filtration includes submerged microfiltration/ultrafiltration and pressurized microfiltration/ultrafiltration.

Furthermore, current state reverse osmosis membranes in some installations  
20 require multiple post treatment stages to achieve the desired product water. These additional stages require additional plant space and energy consumption.

Therefore, there is a need in the art for filtration devices that provide for improved flow characteristics, reduced size and weight and increased operational life while reducing or consolidating the demand for extensive pre-treatment and post treatment.  
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#### SUMMARY OF THE INVENTION

In light of the foregoing, it is a first aspect of the present invention to provide a tunable layered membrane configuration for filtration and selective isolation and recovery devices.

30 It is another aspect of the present invention to provide a tunable membrane configuration for a filtration or selective fluidic isolation and recovery device, comprising a housing having an inlet at one end and an outlet at an opposite end, the housing having an opening extending from the inlet to the outlet, an internal support structure maintained

in the opening, and a layered filtration media carried by the internal support structure, the media separating feedwater received at the inlet into at least three separate output flows.

5 It is still another aspect to provide a device according to the above, wherein the filtration media comprises at least three flow channels, and at least two different planar membranes disposed adjacent two of the at least three channels, the membranes having different tunable selectivity, producing an effective porosity, to filter the feedwater into the at least two outputs/permeates.

10 It is another aspect for the embodiment above to provide the device, wherein the filtration media further comprises a membrane support structure associated with each membrane and carried by the internal support structure.

It is yet another aspect for the embodiment above to provide the device, wherein one of the at least three channels is a first channel having at least one of a first planar membrane on each side thereof.

15 It is still another aspect for the embodiment above to provide the device, wherein one of the at least three channels is a second channel having the membrane support structure on one side and a second planar membrane on an opposite side.

It is a further aspect for the embodiment above to provide the device, wherein one of the at least three channels is a third channel having the membrane support structure on both sides thereof.

20 It is another aspect for the embodiment above to provide the device, wherein the planar membranes are constructed from perforated graphene materials.

25 It is yet another aspect for the embodiment above to provide the device, wherein the planar membrane can be tuned for increased selectivity through pore size or charge characteristics via electric charge or functionalization, or to provide planar membranes capable of carrying electrical charge and that are controlled in such manner to disrupt the effects of concentration polarization at the membrane's surface, or to provide one of the planar membranes for selective isolation or recovery of a specific target in the feedwater by combined use of pore control and electrical charge.

30 It is still another aspect of the selective isolation embodiment to provide pore control and electrical charge in combination to create an effective porosity for increased selectivity of rejection of charged particles in the feedwater.

It is another aspect for the first embodiment above to provide filtration media that comprises planar membranes constructed from perforated graphene, and wherein the planar membranes are configured for multiple stages of filtration including

microfiltration/ultrafiltration and nanofiltration/reverse osmosis in a single device, or multiple stages of one type of filtration with more selective bands.

It is a further aspect for the first embodiment above to provide filtration media that comprises planar membranes constructed from perforated graphene, and wherein the planar membranes are configured for multiple stages of reverse osmosis desalination to achieve product water quality in a single device, using membranes of the same selectivity.

It is still a further aspect for the first embodiment above to provide filtration media that comprises planar membranes constructed from perforated graphene, and wherein the planar membranes are configured for progressively selective stages of reverse osmosis desalination to reduce pressure of each incremental step and corresponding concentration polarization at the membrane's surface.

It is yet a further aspect for the first embodiment above to provide filtration media that comprises planar membranes constructed from perforated graphene, and wherein the planar membranes are configured for selective isolation and recovery of a target particulate, solute, or analyte within one or more of the permeate streams.

It is still a further aspect for the first embodiment above to provide layered filtration media that can be configured in a planar, tubular, or spiral wound configuration.

#### BRIEF DESCRIPTION OF THE DRAWINGS

These and other features and advantages of the present invention will become better understood with regard to the following description, appended claims, and accompanying drawings, none of which are to scale, wherein:

Fig. 1 is a right side enlarged perspective schematic view of a filtration device according to the concepts of the present invention;

Fig. 2 is a left side enlarged perspective schematic view of the filtration device according to the concepts of the present invention;

Fig. 3 is a cross-sectional schematic view of the filtration device showing a filtration media according to the concepts of the present invention;

Fig. 4 is a cross-sectional schematic view showing a membrane in the filtration media where concentration polarization occurs on the surface of the membrane;

Fig. 5 is a cross-sectional schematic view showing the membrane connected to an applied voltage source which disrupts a boundary layer of concentration polarization for charged particles; and

Fig. 6 is a cross-sectional schematic view showing the membrane connected to an

applied voltage source combined with an adjusted membrane aperture size for high flux, high selectivity filtration of charged particles.

### BEST MODE FOR CARRYING OUT THE INVENTION

5 Referring now to Figs. 1 and 2, it can be seen that a filtration device is designated generally by the numeral 10. Fig. 1 presents a general perspective cross-sectional view of an inlet side while Fig. 2 presents a perspective general cross-sectional view of an outlet side of the filtration device. The device 10 includes a housing 12 which may be of a cylindrical construction as shown, but other shapes are believed to be possible depending  
10 upon end-use applications. In any event, the housing 12 includes an inlet 14 which receives feedwater 15 or other fluid for filtration or selective isolation and recovery. Although the term feedwater is used throughout this description, it will be appreciated that the feedwater or fluid material provided to the filtration device may not include water. As used herein, feedwater refers to the medium that includes components supplied to the  
15 filtration device for separation and removal.

Attached to the inlet is an inlet cap 16 which provides for a feedwater pipe 18 so as to allow for the feedwater to be directed into the housing. As will be appreciated by skilled artisans, the inlet cap 16 directs the received feedwater 15 into a plurality of feed channels as will be described. In some embodiments, the cap 16 may have conduits to  
20 direct the feedwater into the feed channels. In other embodiments, the feed channels may be surrounded by a non-porous surface such that the feedwater is directed into the feed channels.

An outlet 22 is disposed at an opposite end of the housing 12 and provides an outlet cap 24. The outlet cap 24 includes at least two exit pipes, a permeate pipe and  
25 concentrate pipe. In another embodiment, the outlet cap includes a permeate pipe 26, an intermediate permeate pipe 28, and a concentrate pipe 30. These pipes, outlet flows or conduits direct the filtered feedwater based upon their properties after filtration, for further use. The outlet cap 24 is configured to maintain the separation of the permeate, the intermediate permeate and the concentrate from each other. It will be appreciated that the  
30 concentrate may also be referred to as a permeate.

Depending on the application, any of the filtrations of the feedwater could include a target product for retrieval or target impurity or contaminant for removal. If only one target permeate is desired, concentrate streams can be combined for disposal or disposed of separately. It may be desired to recover an intermediate concentrate stream, such as a

precious metal recovery, where a middle stage is the product and all other stages or collected for either disposal or reuse. In water recovery applications, typically the final separation produces the filtrate and other stages will be concentrate for disposal. As will be discussed, the layering of membranes and outlet pipes can be scaled for any desired number of concentrate and permeate streams.

Referring now to Figs. 1-3, the housing 12 includes an opening 32 which extends the entire length thereof. Maintained within the housing 12 is an internal support structure 34 which includes various ledges, steps or other structural features so as to support a filtration media designated generally by the numeral 36. Other packaging arrangements are possible including spiral wound or tubular configurations.

The filtration media 36 includes a planar layered configuration which includes at least one feed channel 40, at least one high flux first membrane 42, at least one high flux second membrane 43, at least one membrane porous support structure 44, at least one first permeate spacer 52, and at least one second permeate spacer 54. The alphanumeric designations FC (feed channel 40), M1 (first membrane 42), M2 (second membrane 42), SS (support structure 44), PS1 (permeate spacer 52), and PS2 (permeate spacer 54) are provided in Fig. 3 to provide a clear designation as to each layer. It will be appreciated that although the various layers of filtration media are shown slightly spaced apart for clarity purposes, in practice the various adjacent layers will be in touching contact with one another, with seals as appropriate between membranes, feed channels, and permeate spacers so as to provide separated output flow paths between permeates and concentrates. It will further be appreciated that the membrane and membrane porous support structure can be a single composite membrane. Different positional arrangements of the aforementioned components can be utilized depending upon the components in the feedwater and how the components can best be efficiently separated or filtered from one another. As used herein, the feedwater may contain undesired constituents such as sodium, chlorine, salts, toxins, virus bacteria, and other suspended contaminants of similar size that are carried by a fluid medium such as a solvent or water.

Generally, the feedwater 15 is received by at least one feed channel 40 which delivers the feedwater to a high flux membrane 42 that is supported by the support structure 44. The feed channel 40 may contain a spacer material consisting of either a woven or non-woven material. The feed spacer material is constructed from a polymeric material such as polypropylene, polyethylene, polyester, polyamides, and/or fluoropolymers. Non-polymeric materials possessing desirable hydrodynamic and

application specific properties such as porous ceramics or porous sintered metals, or other materials possessing desirable hydrodynamic and application specific properties may also be used for the feed spacers. The feed channel may have a thickness of between 0.02" to 0.04". Other embodiments may use thicknesses of between 0.02" to 0.20" for the feed channels. The feed channel 40 is configured to allow the feedwater to flow from the inlet toward the outlet. Each membrane support structure includes a plurality of holes 48 such that the structure provides minimal flow resistance. In certain packaging configurations, a feed spacer can function to set a channel height for the feedwater to flow through.

In the present embodiment, the support structure is constructed from polymeric materials such as polycarbonate or polyester, which may be used in conjunction to comprise a laminated or composite backing structure depending on the application. Other materials with similar structural hydrodynamic properties could be used. The holes 48 are sized anywhere between 15 to 200 nanometers in diameter and may be spaced apart from one another depending on hole size used, with it being desirable to use backing material as open as possible to maintain a desirable flow while adequately supporting the membrane. Indeed, a structure 44 having an open area of up to 25% could be used. Other hole sizing and spacing may be used.

In some embodiments the channel height may be sized to accommodate a range of channel spacer designs to receive a mechanical mechanism 57 that generates turbulence of the fluid prior to the feedwater entering the high flux membrane 42. The mechanical mechanisms 57 may include, but are not limited to, ribs or protrusions that are adjacent or integral with the feed channel 40 or feed spacer, if used. Turbulence may also be generated by electrical mechanisms may include, but are not limited to alternating current or direct current charges.

In the present embodiment, each of the high flux membranes 42 and 43 is a graphene membrane as described in U.S. Patent No. 8,361,321, which is incorporated herein by reference. The graphene membrane is a single-atomic-layer-thick layer of carbon atoms, bound together to define a sheet. The thickness of a single graphene membrane, which may be referred to as a layer or a sheet, is approximately 0.2 to 0.3 nanometers (nm). In some embodiments, multiple graphene layers can be formed, having greater thickness and correspondingly greater strength. Multiple graphene sheets can be provided in multiple layers as the membrane is grown or formed, and is commonly known as few layer graphene. Or multiple graphene sheets can be achieved by layering or positioning one graphene layer on top of another. For all the embodiments disclosed



herein, a single layer of graphene or multiple graphene layers may be used. Testing reveals that multiple layers of graphene maintain their integrity and function, possibly as a result of self-adhesion. This improves the strength of the membrane and in some cases flow performance. The perforated graphene high flux throughput material provides significantly improved filtration properties, as opposed to polyamide or other polymeric material filtration materials. In most embodiments, the graphene membrane is 0.5 to 2 nanometers thick. The carbon atoms of the graphene layer define a repeating pattern of hexagonal ring structures (benzene rings) constructed of six carbon atoms, which form a honeycomb lattice of carbon atoms. An interstitial aperture is formed by each six carbon atom ring structure in the sheet and this interstitial aperture is less than one nanometer across. Indeed, skilled artisans will appreciate that the interstitial aperture is believed to be about 0.23 nanometers across at its longest dimension. Accordingly, the dimension and configuration of the interstitial aperture and the electron nature of the graphene precludes transport of any molecule across the graphene's thickness unless there are perforations. This dimension is much too small to allow the passage of either water or ions.

In order to form the perforated graphene membrane, one or more perforations are made. A representative generally or nominally round apertures or perforations 55 are defined through the graphene membrane 42. The graphene membrane 43 will have apertures 56 that are smaller in diameter than apertures 55. For example, aperture 55 may have a nominal diameter of about 1.4 nanometers or a range of diameters of between 1.2 to 1.6 nm, while aperture 56 may have a diameter of about 0.9 nm or a range of between 0.8 to 1.2 nm. The eighth nanometer dimension is selected to block the smallest of the ions which would ordinarily be expected in salt or brackish water, which is the sodium ion. In a similar manner, the 1.2 nanometer dimension is selected to block ions such as divalent ions, which are also found in salt water. To properly filter the feedwater into permeates, the feedwater will be directed through the two or more membranes which have progressively smaller diameters. In the present embodiment, the first membrane would block the divalent ions and the second membrane would block the monovalent ions. The generally round shape of the apertures are affected by the fact that the edges of the aperture are defined, in part, by the hexagonal carbon ring structure of the graphene membrane 42. Other aperture sizes may be selected depending upon the constituents of the feedwater and the constituents or components of the feedwater that is desired to be blocked or filtered. Accordingly, the apertures 55 and 56 may range in size from 0.5 nm to 1.2 nm in some embodiments, or from 1.0 to 10 nm in other embodiments. And in other embodiments, the

size of the apertures 55 and 56 may range from 10 nm to 100 nm.

Apertures in the graphene membrane may be made by selective oxidation, by which is meant exposure to an oxidizing agent for a selected period of time. It is believed that the apertures 55/56 can also be laser-drilled. As described in the publication Nano Lett. 2008, Vol.8, no.7, pg 1965-1970, the most straightforward perforation strategy is to treat the graphene film with dilute oxygen in argon at elevated temperature. As described therein, through apertures or holes in the 20 to 180 nm range were etched in graphene using 350 mTorr of oxygen in 1 atmosphere (atm) argon at 500°C for 2 hours. The paper reasonably suggests that the number of holes is related to defects in the graphene sheet and the size of the holes is related to the residence time. This is believed to be the preferred method for making the desired perforations in graphene structures. The structures may be graphene nanoplatelets and graphene nanoribbons. Thus, apertures in the desired range can be formed by shorter oxidation times. Another more involved method as described in Kim et al. "*Fabrication and Characterization of Large Area, Semiconducting Nanoperforated Graphene Materials*," Nano Letters 2010 Vol. 10, No. 4, March 1, 2010, pp 1125-1131 utilizes a self assembling polymer that creates a mask suitable for patterning using reactive ion etching. A P(S-blockMMA) block copolymer forms an array of PMMA columns that form vias for the RIE upon redeveloping. The pattern of holes is very dense. The number and size of holes is controlled by the molecular weight of the PMMA block and the weight fraction of the PMMA in the P(S-MMA). Either method has the potential to produce perforated graphene sheets. Other methods of forming the apertures may be employed. In the embodiments disclosed herein, it will be appreciated that the apertures are sized to block selected components of the feedwater and allow passage of other components. Moreover, the edges of the apertures may be modified to assist in blocking or passing of selected components.

Although graphene is an exemplary material for use as the high flux membrane 42/43, skilled artisans will appreciate that other materials such as boron nitride, metal chalcogenides, silicene and germanene, and molybdenum disulfide offer two dimensional thinness, although use of these materials for filtration applications is not known to be as ideal as graphene. In any event, the membranes 42/43 function to preclude passage of unwanted components of the feedwater while allowing the desired components to pass therethrough and, accordingly through the support structure 44 by virtue of structure holes 48 provided therethrough. After passing through the first support structure 44, the fluid material flows into the first permeate spacer 52. Underneath the spacer 52 is the second

membrane 43 which is supported or carried by another underlying support structure 44. Fluid that flows through the underlying support structure 44 is then received into the second permeate spacer 54. In the present embodiment, both sides of the permeate spacer 54 are adjacent to support structures 44. This layered construction is repeated as shown or  
5 as needed to filter the feedwater into the desired concentrate and permeates. In the present embodiment, the permeate spacer 52 is constructed and sized for compressive loads which will have a substantially different magnitude from those of the feed spacer 42 for high pressure operation. The purpose of the permeate spacers differs as it primarily provides structural support to the membrane and does not generally serve to produce flow  
10 turbulence as does the feed spacer. The permeate spacer also provides a conduit for permeate flow from the back side of the membrane to a common permeate collection means. Skilled artisans will appreciate that construction and sizing of the permeate spacer may be varied depending upon the characteristics of the feedwater and therefore the operating pressure and permeate flux rate.

15 In the embodiment shown in Fig. 3, the uppermost membrane support structure 44 supports the first membrane 42. The filtered material flows through the membrane 42 and the membrane support structure 44 and it is received by the permeate spacer 52. Disposed on the underside of the spacer 52 is the other membrane 43 which is supported by another support structure 44. Disposed between that support structure and another like structure is  
20 the spacer 54. With the spacer 54 as a middle component, a reverse ordering of layers is provided: a second membrane 43, spacer 52, support structure 44, membrane 42, and the feed channel 40. These planar layers are configured so as to provide the desired material flows. Flow through the device moves from the input side to the output side down the length of the housing, with permeate flows moving down the corresponding permeate  
25 channels, tangential to the corresponding membrane surfaces. The flow direction is in and out of the page as viewed in Fig. 3. The directional arrows provided in Fig. 3 are for the purpose of showing how the feedwater flows from one layer to another.

The filtration media 36 is configured to optimize the relationship of the various layers with one another. As such, each feed channel 40 has at least one membrane on one  
30 side thereof, and in some instances both sides. A spacer may be provided between membranes that are adjacent one another. Each permeate spacer 52 has a support structure 44 on one side and a first membrane 42 on an opposite side. Each second membrane 43 has a permeate spacer 52 on one side and a support structure 44 on an opposite side. Each permeate spacer 54 has a support structure 44 on both sides. Finally, each membrane 42 is

positioned between a support structure 44 on one side and a feed channel on an opposite side. The filtered material that collects in the permeate spacer 52 then flows out the housing through the permeate pipe 26. The filtered material that collects in the permeate spacer 54 then flows out the housing through the permeate pipe 28. The unfiltered or blocked material that remains in the feed spacers flow out the housing through the concentrate pipe 30.

As skilled artisans will appreciate, the channels 40, the spacers 52, and 54, and the membranes 42 and 43 are of a planar construction. In other words, each are provided with a width and length which receives the feed supply and the filtered fluid. In the present embodiment the support structure 44, along with the membranes 42 which they support, are removable from the housing by virtue of their retention by the internal support structure 34. The support structure 44 includes a lateral edge 74 along each side that provides a handle 75. Each handle 75 includes a groove 76. Each groove 76 is slidably receivable on a corresponding ridge 34. Additionally, an underside of each handle 75 may be slidably received on a corresponding ledge 35. The support structure 44 can be mechanically fastened to the internal support structure -- ridges 34, ledges 35 -- to maintain pressure during operation. Unfastening of the support structures allows access to the spacers and membranes located inside the housing. In other embodiments the construction may be spiral wound, or other geometries where multiple passes are achieved. As previously discussed, the membranes 42 and 43 may be high flux throughput material.

Adjacent layers may be specifically associated with one another. For example, a layered sequence of a first membrane 42, a support structure 44, a permeate spacer 52, a second membrane 43, another support structure 44, a permeate spacer 54, yet another support structure 44, another second membrane 43, another permeate spacer 52, still another support structure 44, and another first membrane 42 could be configured so as to form a membrane leaf structure. The leaf structure, which may have any number of different membranes with different aperture diameters, could be removed and replaced as needed. The associated support structures could be secured to one another as needed.

In one embodiment, the membranes are constructed from the perforated graphene material with a number of enabling tunable characteristics including pore size control through use of various perforation techniques, examples of which have been described above, and charge, electrical or chemical modifications, as described in U.S. Patent Application Serial No. 13/422,753 for Functionalization of Graphene Holes for

Deionization, which is incorporated herein by reference. A layered graphene based membrane can be made with macro sized sheets of graphene joined to a support porous backing or by micro size platelets deposited on a porous backing so as to effectively create a solid graphene filtration layer on said backing. In all cases, the graphene is porous so as to allow flow of desired fluids. In some cases, graphene as grown with nano-scaled imperfections may be suitable for certain applications.

In some embodiments, a switched voltage supply 78, which is maintained outside the housing but could be within the housing, is connected to the membranes 42 and/or 43 by a pair of conductors 80. In most embodiments, the conductors are attached at diametrically opposite ends of the respective membranes 42 and 43. As skilled artisans will appreciate, application of an electrical voltage to a membrane 42 or 43 that is graphene or has some other electrically conductive material generates a repulsive force that causes turbulence that is transmitted or transferred to the feedwater, in particular the polarized salt ions within the feedwater. In some embodiments, the forces will be alternated between repulsive and attractive to produce maximum turbulence. This turbulence assists in moving the permeate and condensate away from the membrane's surface and through the various layers. In the perforated graphene embodiment, the material is able to conduct an electrical charge which can be controlled to disrupt concentration polarization, thereby lowering operating pressure.

As feedwater flows through the membrane and salts are rejected by the membrane, as seen in Figs. 4-6, a boundary layer is formed near the membrane surface in which the salt concentration exceeds the salt concentration in the bulk solution. This increase of salt concentration is called concentration polarization. The effect of concentration polarization is to reduce actual product water flow rate and salt rejection versus theoretical estimates. As shown in Fig. 4, an exemplary membrane 42/43 and channel 40/52 is shown along with a representation of concentration polarization that occurs as the blocked ions or particulates, which is identified as "ion/particle buildup" in Figs. 4-6 and schematically represented as dots, accumulate near the apertures 55 and toward the rear of the flow area. The layer 84, if left in place, can effectively block or clog the apertures. As such, use of the switchable voltage supply 78, which may be connected to any one or all of the membranes 42/43 is beneficial in repelling the blocked ions and in maintaining flow of the concentrate and permeates through the filtration media as represented in Fig. 5. Furthermore, the electrical charge carrying capability provided by the supply 78 can be combined with pore size control on at least one layer to increase selectivity of salt

rejection in the membrane as shown in Fig 6. Pore size control allows for use of enlarged apertures 55' which permits higher flow through the membrane while still adequately blocking the ions/particulates of interest. In another embodiment, charge characteristics could be achieved through chemical functionalization which is described in previously mentioned U.S. Patent Application Serial No. 13/422,753. In a water filtration application with perforated graphene, separation can be achieved through a single layer in which rejection control is tuned through pore size control, or a combination of pore size control and charge characteristics for the required selectivity. Furthermore, concentration polarization effects can be mitigated with use of electrical charge to disrupt the boundary layer effects experienced with current state of art polymeric membranes as shown in Fig 6.

The high flux throughput material provides significantly improved filtration properties, as opposed to polyimide or other polymeric material filtration materials. In most embodiments, the graphene material is 0.3 to 5 nanometers thick. Regardless of the thickness or type of material used, the membranes 42 and 43 will be provided with different porosity so as to selectively pass and/or block components in the feedwater. For example, using a layered planar design, the membrane 42 can be configured with porosity suitable to perform ultrafiltration and reject particles in the 5-100 nanometers or greater range including colloids, proteins, microbiological contaminants, and large organic molecules. The concentrate will be retained by the first membrane in the stack, while the permeate, still including monovalent and divalent salts, will pass to the second membrane surface. The second high flux membrane will be configured with a porosity suitable for salt rejection and reject all salts above approximately 1 nanometer, allowing only pure water to pass through. This will result in two reject streams that can be harvested separately if desired, and one product water stream for each membrane stack. This example is for two stages of rejection in a dual membrane stack. Depending on the need, this stack can be expanded for multiple stages of rejection. This concept can also be used for multi-stages of reverse osmosis for refined rejection (improved salt rejection, boron rejection) and improved output water quality if needed. Furthermore, this concept can be used for progressively selective salt filtration, meaning each layer is tuned for increasing selectivity of salt rejection. This enables incremental salt removal at lower pressures in each step, mitigating concentration polarization and associated pressure inefficiencies and material structural loading.

In another embodiment, the tunable membrane configuration can be used to selectively recover a particulate, solute, or analyte of interest. The substance can be

targeted for its value as a product such as a precious metal, or the importance of isolating it for disposal such as contaminant. In this case the first membrane will be tuned or sized to reject all substances larger than the target substance, allowing the target substance and all substances smaller to pass through. The second membrane will be tuned or sized to block the target substance, allowing all smaller substance to pass through and selectively isolating the substance of interest. Again, in the perforated graphene embodiment the use of electrical charge can further be used to increase the selectivity of flux at which the filtration or recovery process occurs. As used herein, tunable selectivity is the ability to control the specific solutes or particles that a membrane rejects, recovers or isolates based on physical size via membrane pore control, with the option to supplement by use of material functionalization of the hole periphery or applied electrical charge to a conductive membrane.

In the present embodiment the membrane support structures 44, along with the membranes 42 and 43 which they support, are removable from the housing by virtue of their support by the internal support structure 34 and 35.

The filtration media 16 can be configured with the various layers disclosed and selection of membrane aperture sizes to provide microfiltration, ultrafiltration, nanofiltration, and reverse osmosis in a single media and/or multiple stages of one type of filtration with more selective bands of filtration by using progressively smaller aperture sizes in each membrane. In another embodiment, the filtration media can be configured to provide multiple states of reverse osmosis desalination to achieve product water quality in a single device using membranes of the same selectivity. In yet another embodiment, the filtration media can be configured to provide progressively selective stages of reverse osmosis desalination to reduce pressure of each incremental step and corresponding concentration polarization at the membrane's surface.

The membrane configuration shown in filtration device 10 has several readily apparent advantages. By utilizing ultra thin or two dimensional materials, it provides for consolidation of multiple levels of filtration in a single device design. The design may be a layered planar design, spiral wound design, or other geometry that accommodates multiple passes. The consolidation of filtration stages reduces the overall size required for a filtration operation. Indeed, use of a high flux throughput material, such as a perforated graphene material, allows for a reduction in volume and weight by a factor of anywhere between five to fifty times. Still yet another advantage of the filtration device 10 is that it allows for multiple devices to be attached in series to provide additional filtering as

needed. Another advantage is that the tunable membrane design allows for “tuned” filtering of the feed supply. In other words, selective materials can be separated for a desired end use be it disposal or use. Furthermore, with perforated graphene the use of electrical charge can be incorporated to further improve selectivity and flux during the filtration or recovery operation.

Thus, it can be seen that the objects of the invention have been satisfied by the structure and its method for use presented above. While in accordance with the Patent Statutes, only the best mode and preferred embodiment has been presented and described in detail, it is to be understood that the invention is not limited thereto or thereby. Accordingly, for an appreciation of the true scope and breadth of the invention, reference should be made to the following claims.



CLAIMS

What is claimed is:

- 1       1.     A tunable membrane configuration for a filtration or selective fluidic isolation and  
2             recovery device, comprising:  
3                 a housing having an inlet at one end and an outlet at an opposite end, said  
4             housing having an opening extending from said inlet to said outlet;  
5                 an internal support structure maintained in said opening; and  
6                 a layered filtration media carried by said internal support structure, said  
7             media separating feedwater received at said inlet into at least three separate output  
8             flows.
- 1       2.     The device according to claim 1, wherein said filtration media comprises:  
2             at least three flow channels; and  
3             at least two different planar membranes disposed adjacent two of said at  
4             least three flow channels, said membranes having different tunable selectivity,  
5             producing an effective porosity, to filter the feedwater into the at least two  
6             outputs/permeates.
- 1       3.     The device according to claim 2, wherein said filtration media further comprises:  
2             a membrane support structure associated with each said membrane and  
3             carried by said internal support structure.
- 1       4.     The device according to claim 3, wherein one of said at least three channels is a  
2             first channel having at least one of a first planar membrane on each side thereof.
- 1       5.     The device according to claim 4, wherein one of said at least three channels is a  
2             second channel having said membrane support structure on one side and a second  
3             planar membrane on an opposite side.
- 1       6.     The device according to claim 5, wherein one of said at least three channels is a  
2             third channel having said membrane support structure on both sides thereof.

- 1       7.       The device according to claim 2, wherein said planar membranes are constructed  
2               from perforated graphene materials.
- 1       8.       The device according to claim 7, wherein said planar membrane can be tuned for  
2               increased selectivity though pore size or charge characteristics via electric charge  
3               or functionalization.
- 1       9.       The device according to claim 7, wherein said planar membranes are capable of  
2               carrying electrical charge and are controlled in such manner to disrupt the effects  
3               of concentration polarization at the membrane's surface.
- 1       10.      The device according to claim 7 wherein one of said planar membranes is used for  
2               selective isolation or recovery of a specific target in said feedwater by combined  
3               use of pore control and electrical charge.
- 1       11.      The device according to claim 10 , wherein pore control and electrical charge can  
2               be combined to create an effective porosity for increased selectivity of rejection of  
3               charged particles in said feedwater.
- 1       12.      The device according to claim 1, wherein said filtration media comprises planar  
2               membranes constructed from perforated graphene, and wherein said planar  
3               membranes are configured for multiple stages of filtration including  
4               microfiltration/ultrafiltration and nanofiltration/reverse osmosis in a single device,  
5               or multiple stages of one type of filtration with more selective bands.
- 1       13.      The device according to claim 1, wherein said filtration media comprises planar  
2               membranes constructed from perforated graphene, and wherein said planar  
3               membranes are configured for multiple stages of reverse osmosis desalination to  
4               achieve product water quality in a single device, using membranes of the same  
5               selectivity.
- 1       14.      The device according to claim 1 wherein said filtration media comprises planar  
2               membranes constructed from perforated graphene, and wherein said planar  
3               membranes are configured for progressively selective stages of reverse osmosis

4 desalination to reduce pressure of each incremental step and corresponding  
5 concentration polarization at said membrane's surface.

1 15. The device according to claim 1, wherein said filtration media comprises planar  
2 membranes constructed from perforated graphene, and wherein said planar  
3 membranes are configured for selective isolation and recovery of a target  
4 particulate, solute, or analyte within one or more of the permeate streams.

1 16. The device according to claim 1, wherein said layered filtration media can be  
2 configured in a planar, tubular, or spiral wound configuration.

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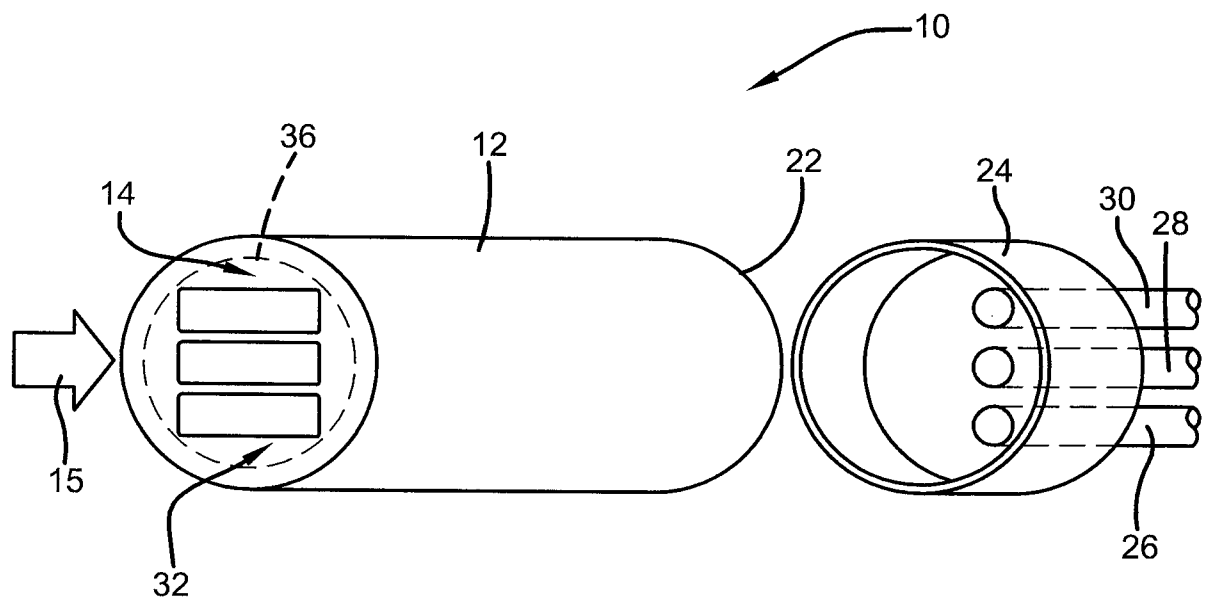


FIG. 1

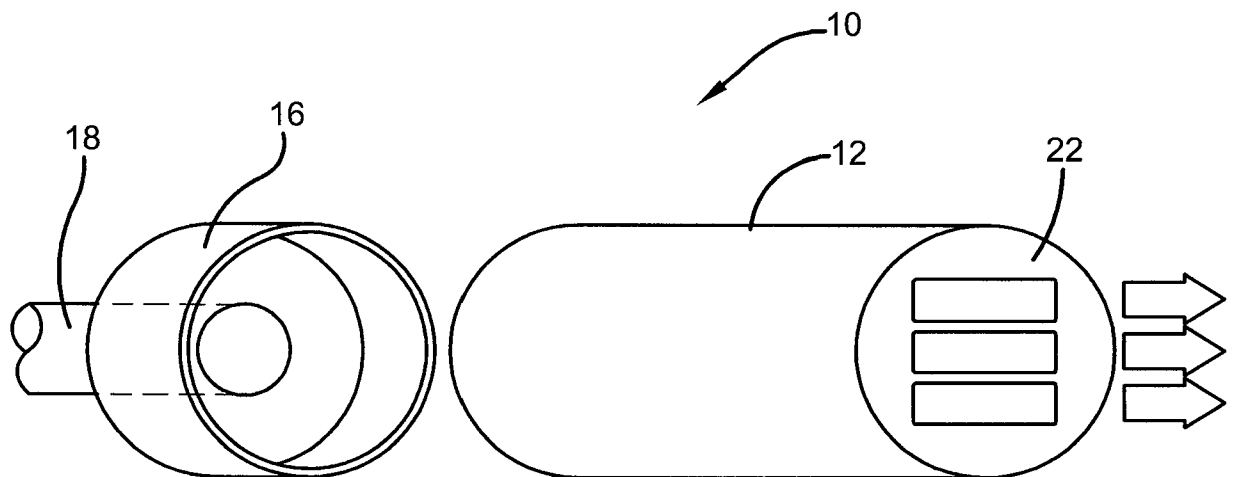
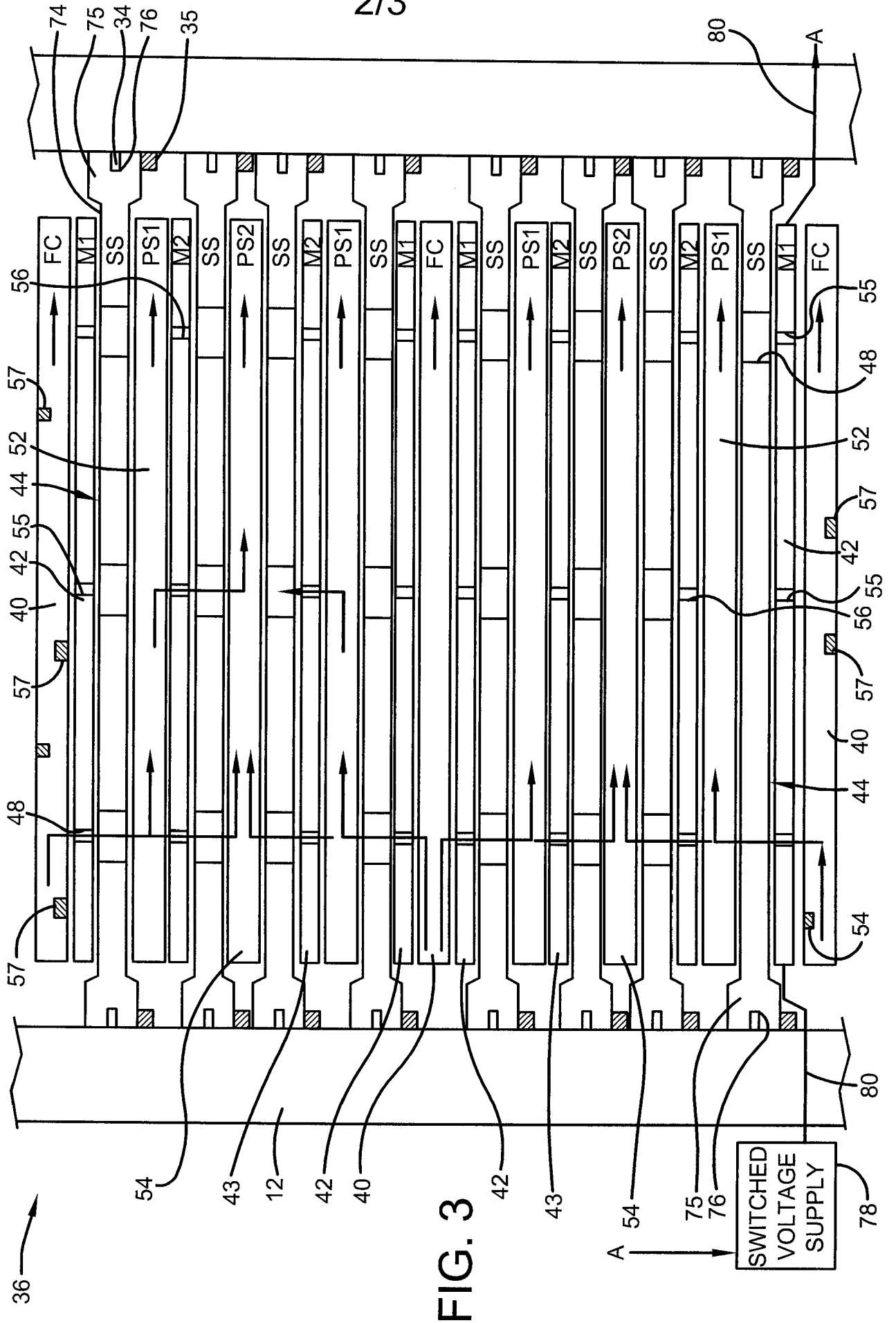


FIG. 2



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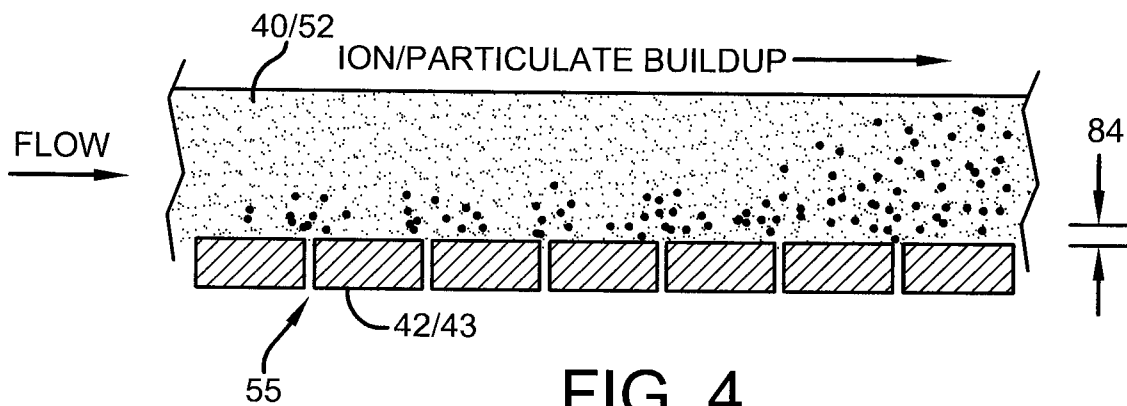


FIG. 4

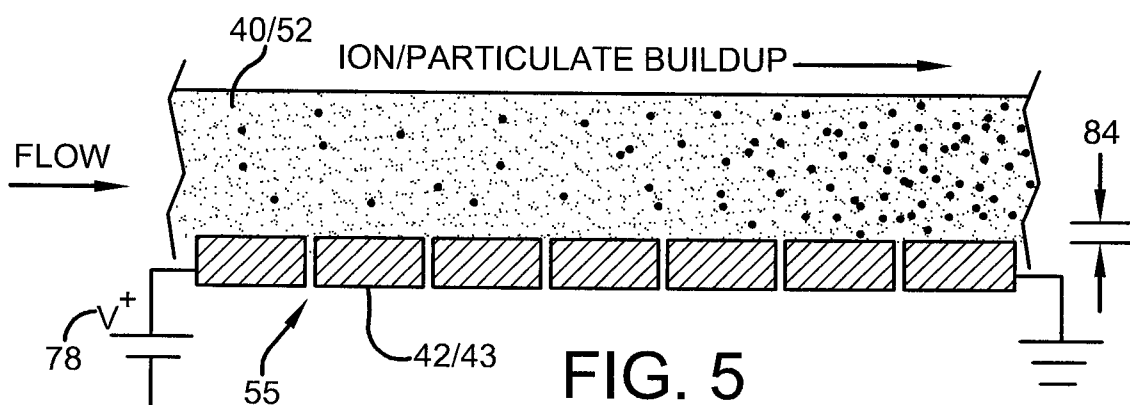


FIG. 5

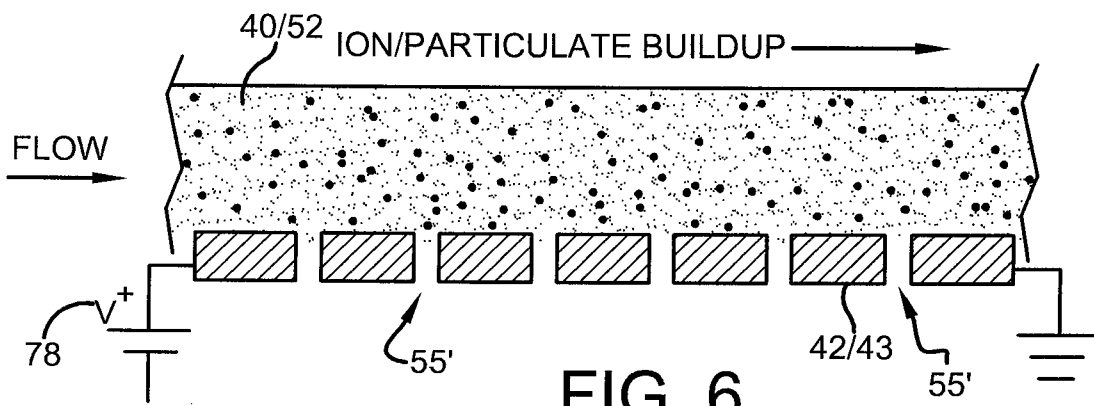


FIG. 6

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2013/033403

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	B01D61/02	B01D61/12
	B01D71/02	B01D63/08
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		B01D69/06
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
B01D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/048804 A1 (STETSON JOHN B [US] ET AL) 1 March 2012 (2012-03-01)	1-8,12, 14-16
Y	paragraphs [0021], [0027]; figures 2,4, 6	9-11,13
Y	----- KR 2012 0022164 A (UNIV YONSEI IACF [KR]) 12 March 2012 (2012-03-12)	13
A	paragraph [0032] - paragraph [0040]; claim 13; figures	1-3
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A	page 22, line 16 - page 23, line 6	8,10,11
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	claims 1,7,19; figure 3	
	----- -/-	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
14 June 2013		28/06/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer  Goers, Bernd

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International application No

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A	figures 11-17 -----	8
A	WO 2009/129984 A1 (NTNU TECHNOLOGY TRANSFER AS [NO]; LIE JON ARVID [NO]; BORGE TONE [NO];) 29 October 2009 (2009-10-29) page 3, line 3 - line 8 page 11, line 26 - page 12, line 24 -----	7-11
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