(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
23 June 2022 (23.06.2022)

(10) **International Publication Number**
WO 2022/129819 A1

(51) **International Patent Classification:**
G01N 27/42 (2006.01) ***C02F 1/469*** (2006.01)
G01N 33/18 (2006.01) *G01N 27/30* (2006.01)

(21) **International Application Number:**
PCT/GB2020/053209

(22) **International Filing Date:**
14 December 2020 (14.12.2020)

(25) **Filing Language:** English

(26) **Publication Language:** English

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

(54) **Title:** METHOD FOR DETECTING IONS IN SOLUTION USING A CAPACITIVE DEIONISATION CELL

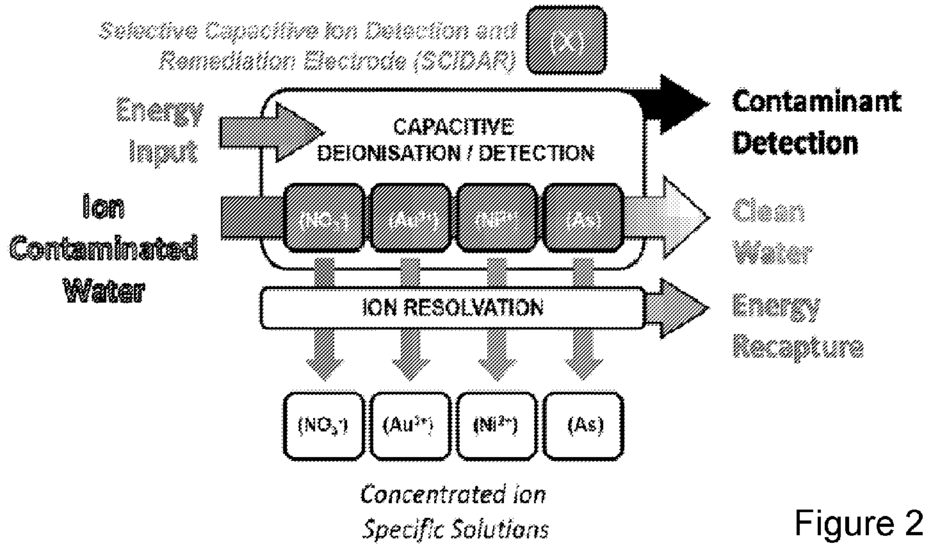


Figure 2

(57) **Abstract:** Method of detecting the concentration of an ion in a solution, comprising the step of providing a capacitive deionisation cell comprising a working electrode formed of a high surface area conductive material (e.g. carbon or graphene aerogels/xerogels), wherein the high surface area conductive material is functionalised with ion specific binding sites. A means for determining the capacitive charging current and voltage on the working electrode is also provided. The concentration of ions in the solution is determined from the changes in the charging current and voltage over time following application of potential across the working electrode in the solution. The application also relates to ion concentration detection devices and systems for detecting ion concentration in a solution.

[Continued on next page]

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

METHOD FOR DETECTING IONS IN SOLUTION

FIELD OF THE INVENTION

The present invention relates to a method of detecting the presence of an ion in a solution using a capacitive deionisation cell comprising a working electrode formed of a high surface area conductive material functionalised with ion specific binding sites. The invention is also directed to ion concentration detection devices and systems for detecting ion concentration in solution.

BACKGROUND TO THE INVENTION

Water contaminated with ions from sources such as heavy metals and fertilisers causes a wide range of environmental and health problems around the world. For example, Arsenic (As) is a contaminant that is ubiquitous in the environment and the two soluble forms, arsenite (As^{III}) and arsenate (As^{V}), are toxic. Human activity has resulted in widespread contamination of both soluble forms and As^{III} is prevalent in anoxic environments, including most sources of drinking water. Over 140 million people in 70 countries drink water contaminated with this known carcinogen, and it has been reported to lead directly to the deaths of over 40,000 Bangladeshis each year [1]. Other countries affected include India, Vietnam, USA, Germany, France, Hungary, Australia, Argentina, Mexico and Canada.

Other aqueous ionic pollutants have potential economic value. For example, precious metals such as gold found in mine waste streams, jewellery manufacturing waste streams, electroplating plant waste streams, tailings and urban wastewater. However, research efforts have been focused on the contamination of heavy metals and toxic metals with little focus on precious metals [2].

Reliable detection of pollutant ions in solution is a cornerstone of effective environmental and public health protection strategies. The application of such technology would enable accurate monitoring of contamination levels which would ultimately help direct both decontamination and pollution prevention efforts. Furthermore, the detection and subsequent collection of valuable metals in usable form would facilitate the emergence of circular economies, and provide resources to promote the implementation of this clean-up technology.

Previous methods used for ion detection in solution have used Ion Selective Electrodes (ISE's). Ion selective electrodes rely on the potential differences arising between the target solution and a reference solution. Ion selectivity is achieved with use of ion-exchange membranes on the electrodes, which ideally allow the uptake of only one specific ion. Redox processes do not occur at ISEs, and instead, the potential developed at the membrane is the result of ion exchange or ion transport processes occurring at the interface between the membrane and solution. However, these devices have various shortcomings. They suffer from slow kinetics, take a long time to reach equilibrium, and they exhibit operational issues under long term remote usage. In particular, they experience 'calibration drift' that results in inaccurate readings. The devices also generally require daily recalibration, which is time consuming, costly and inefficient.

As such, there is a need for improved methods and devices for effective detection and remediation of metals in solutions such as brackish water, sea water, municipal sewer waste, industrial waste streams, acid mine drainage and biological samples. There is also a need to develop reliable ion detection methods that can provide real-time, continual remote monitoring of ions in solution, which would aid in the detection of contaminant spillage. Further, given the toxicity of various heavy metal ions at very low concentrations, there is also a need to develop ion detection methods that are particularly sensitive to specific ions at dilute concentrations.

SUMMARY OF THE INVENTION

The present inventors have developed a new method for ion detection that integrates ion collection. They have invented Selective Capacitive Ion Detection and Remediation (SCIDAR) electrodes for capacitive deionisation cells that are specific to particular ions. Thus, an electrode has been developed that has the ability to capacitively adsorb specific ions and then discharge the ions into solution, allowing the capacitive sensor to be reused.

Accordingly, in a first aspect, the present invention provides a method for detecting the concentration of an ion in a solution. The method involves the steps of providing a capacitive deionisation cell comprising a working electrode formed of a high surface area conductive material. The high surface area conductive material is functionalised with ion specific binding sites. A means for detecting the capacitive charging current and voltage on the working electrode is also provided. The presence or concentration of ions in solution is determined from the changes in the charging current and voltage over time following application of potential across the working electrode in the solution.

According to a second aspect, the present invention provides a device for detecting ion concentration in a solution. The device comprises a working electrode comprising a carbon nanotube network that is an aerogel or xerogel. The carbon nanotube network is functionalised with ion specific binding sites.

According to a third aspect, the present invention provides a system for detecting an ion concentration in a solution. The system includes a reservoir comprising a solution; a capacitive deionisation cell comprising a working electrode formed of a high surface area conductive material. The high surface area conductive material is functionalised with ion specific binding sites. The system also comprises a means for determining the capacitive charging current and voltage on the working electrode following application of potential across the working electrode in the solution.

DESCRIPTION OF THE FIGURES

Figure 1 is a schematic showing the operation of a capacitive deionisation (CDI) cell. Upon charging of the cell, ions are drawn electrostatically to electrodes of opposite charge. Once the charge is released, the ions are released back into the water. By holding the cell in a charged state, ions are separated from water leaving cleaner water.

Figure 2 is a schematic showing the overall process of ion pollutant detection using a selective capacitive ion detection and remediation (SCIDAR) electrode.

The detection technology also allows for the recovery for the pollutant ions in separate concentrated solutions. Accordingly, this may also act as an environmental remediation technology.

Figure 3 shows CAD software designs of a simple capacitive deionisation cell where; a) shows the well and lid which can be clamped together. The lid has openings for the electrodes to be inserted; b) shows the electrode holders; and c) represents how the electrode holders slot into the well.

DETAILED DESCRIPTION

Capacitive deionisation (CDI) processes for ion detection and remediation offer various advantages over conventional ion selective electrode systems. They have a higher degree of modularity, and do not require the use of chemicals for regeneration. Redox-active materials are particularly promising for ion adsorption due to their molecular selectivity and electronic tunability. Figure 2 is a schematic showing the overall process of ion pollutant detection using the selective capacitive ion detection and remediation (SCIDAR) electrode of the invention. Energy is applied to the working SCIDAR electrode, resulting in the charging of the system by electrosorption of specific ions by the SCIDAR electrode from contaminated water. This ultimately cleans the water of particular ionic contaminants. Following this, contaminant detection technology enables the detection of specific ions in the contaminated water. If the voltage is removed and the system discharged, ions which were electrostatically drawn to the SCIDAR electrode are discharged back into the solution. This allows for the resolvation of pollutant ions in separate concentrated solutions following discharging of the SCIDAR electrode. As energy is stored during the charging process, some energy may also be recaptured during the ion resolvation process. Following discharging, the capacitive sensor may also be reused.

This method of the SCIDAR system has the advantage that it can measure the cumulative capacitive charge developed within the working SCIDAR electrode, rather than relying on an instantaneous electric potential, as developed in ISEs.

The timescale of the capacitive measurement can also be adjusted to suit different concentration ranges.

In a first aspect, the present invention provides a method for detecting the concentration of an ion in a solution. The method involves the steps of providing a capacitive deionisation cell comprising a working electrode formed of a high surface area conductive material. The working electrode is functionalised with ion specific binding sites. A means for detecting the capacitive charging current and voltage on the working electrode is also provided. The concentration of ions in solution is determined from changes in the charging current and voltage over time following application of potential across the working electrode in the solution.

Preferably, the method involves the steps of providing a capacitive deionisation cell comprising a working electrode formed of a conductive carbon network. The carbon network is functionalised with ion specific binding sites. A means for detecting the capacitive charging current and voltage on the working electrode is also provided. The concentration of ions in solution is determined from changes in the charging current and voltage over time following application of potential across the working electrode in the solution.

The concentration measurements may be based on potentiostatic analysis, which involves sweeping the voltage and observing the effects on the current. Alternatively, the concentration measurements may be based on galvanostatic analysis, which involves sweeping the current and observing the effects on the voltage.

The capacitive deionisation cell may comprise two electrodes in total. Preferably, one of the electrodes is the SCIDAR working electrode. The SCIDAR electrode may be the anode or the cathode, depending on whether it is set up to detect and/or capture cations or anions. A two-electrode cell may also comprise two different SCIDAR electrodes, which are functionalised with different ion specific binding sites specific to capture both anions and cations.

In a two electrode set-up, the charging current is measured across the whole cell and can operate with just a voltage and current measurement, in a similar way to a capacitor. The charge on the electrodes is proportional to the potential difference across the two electrodes. The capacitance C can be defined as:

$$C = \frac{Q}{V}$$

Where C is the capacitance in Farad, Q is the charge in coulombs and V is the voltage difference between the electrodes.

In such two-electrode devices, no potentiostatic voltage control is required, providing a significant advantage over existing systems. The voltage/current relationship is governed by the following equation:

$$I(t) = \frac{dQ(t)}{dt} = C\frac{dV(t)}{dt}$$

Where I is the capacitive current in amperes, Q is the charge in coulombs, C is the capacitance in Farad, V is the voltage in volts and t represents time in seconds.

The capacitive deionisation cell may also use a three electrode set-up which further comprises a reference electrode.

The capacitive deionisation cell may comprise a potentiostat, enabling the charging current of the working SCIDAR electrode to be measured while the potential is controlled. The term “potentiostat” takes its usual definition in the art, and it comprises an electric circuit which controls the potential across the cell by sensing changes in its resistance and accordingly varying the current supplied to the system.

The variable output of electric current of a potentiostat can be described according to the following equation:

$$I_o = \frac{E_c}{R_V}$$

Where I_o is the output electric current of the potentiostat in amperes, E_c is the voltage in volts that is kept constant and R_v is the electrical resistance in ohms that varies.

The potentiostat may be connected to the working SCIDAR electrode, reference electrode and counter electrode in an electrochemical cell. The reference electrode acts as a reference in controlling the working electrode potential, without passing any current, and has a constant electrochemical potential at low current density. The reference electrode may be any standard reference electrode which has a stable and established electrode potential. For example, the reference electrode may be a standard hydrogen electrode, normal hydrogen electrode, reversible hydrogen electrode, copper-copper(II) sulfate electrode, silver-silver chloride electrode and a palladium-hydrogen electrode, among others. The counter electrode injects current into the cell to balance the current observed at the working electrode. It may swing to extreme potentials in order to maintain the voltage. Preferably, the counter electrode has a sufficient surface area to avoid large compliance voltages. Typically, the counter electrode is formed of carbon. The counter electrode may be formed of a similar conductive material to the working electrode, but without the surface chemistry or with a different chemistry.

A potentiostat typically comprises an electrometer to measure the voltage difference between the working and reference electrode, and provides feedback signal within the potentiostat. It also comprises a current to voltage (I/E) converter to measure the current of the cell, and a control amplifier to compare the measured cell voltage to the desired cell voltage and drive current into the cell to force the voltages to be the same.

The capacitive deionisation cell of the invention may comprise a galvanostat, enabling the voltage of the cell to be measured while the current is kept constant. The term “galvanostat” takes its usual definition in the art, and is defined as a device capable of increasing or decreasing the potential over two points in a solution by applying a stable electron current.

The galvanostat may be connected to the working SCIDAR electrode, reference electrode and counter electrode in an electrochemical cell. The galvanostat controls the current flow between the working SCIDAR electrode and the counter electrode, and typically comprises a differential amplifier which measures the potential difference between the reference electrode and working electrode.

The capacitive deionisation cell may comprise a single instrument which can perform as a potentiostat or a galvanostat, depending on its configuration.

Preferably, the capacitive deionisation cell functions with potentiostatic control. In this way, modest operating voltages may be selected, which mitigates unwanted redox reactions occurring with the ions in solution.

Optionally, the capacitive deionisation cell of the present invention may comprise a current collector. The term “current collector” refers to a component of the capacitive deionisation cell that conducts electricity between the working part of the electrode and the terminals of the cell. It may be formed of graphite, copper or aluminium. It may take the form of a sheet, plate, foil or mesh.

Figure 1 illustrates the basic principle of capacitive deionization (CDI) for removing dissolved ions from aqueous solutions. An electrical field is applied between a pair of porous electrodes with a separator in between. The separator in this case is polluted water. The electrode material used typically includes activated carbon, graphene, carbon nanotubes, carbon aerogels and carbon xerogels due to their intrinsic low resistivity, high conductivity and high surface area. The high surface area and accessible pores of the electrodes increases the charge storage capacity of the CDI cell, enabling effective and rapid accumulation of ions.

Upon the application of voltage to the cell, the system ‘charges’ and positive ions are drawn to the cathode while negative ions are drawn to the anode. In this way, ions are segregated and removed from solution based on their charge. If the voltage is removed and the system discharged, ions which were electrostatically drawn to the electrodes are discharged back into the solution. By holding the cell in a charged state, ions are separated from the solution resulting in cleaner water with ionic contaminants removed. However, CDI is not selective and therefore does not discriminate between ions of interest and those with no effects on human or environmental health. Furthermore, it is unable to distinguish between ions of commercial value compared to those of none. The basic purpose of CDI is generally for desalination to create water for irrigation. Usually, CDI cannot be performed at low ion concentration due to the low ion conductivity.

To overcome these issues with selectivity, and reduced functionality in solutions with low ion conductivity, the present inventors have invented a surface functionalised SCIDAR electrode for the co-ordination and electrochemical retention of ions of commercial or environmental interest. The working SCIDAR electrode of the invention comprises a high surface area conductive material which is functionalised with ion specific binding sites. Preferably, the working SCIDAR electrode is formed of a conductive carbon network functionalised with ion specific binding sites. Thus, the SCIDAR electrode of the invention can be designed to selectively bind specific pollutant ions upon the application of potential to the electrode. As the electrode specifically binds ions of interest, the selective current from these ions can be determined, and any background ion concentration can be used to provide conductivity to the cell. The SCIDAR electrode can therefore function at low ion concentrations as it selectively adsorbs dilute pollutant ions of interest while retaining ion conductivity from background ions. This provides a significant advantage over existing CDI cells, which are unselective and cannot usually function at low ion concentrations due to the low ion conductivity.

The integrated capacitive current is measured over time following calibration of the system. The concentration of ions in solution may be determined by comparing the capacitance of the functionalised working electrode to the capacitance of an unfunctionalised reference device. To determine the concentration of the specific ion of interest in solution, the difference in capacitance of the functionalised and unfunctionalised device is compared to the pre-determined selectivity of the working electrode. This way, any variations in background ion concentration are taken into account.

With solutions comprising dilute concentrations of specific ions, potential may is applied to the working SCIDAR electrode over a period of time. The potential may then be removed causing the adsorbed ions to be released, and then potential is quickly reapplied to the working SCIDAR electrode to recapture the specific ions before they have diffused away. Therefore, the charging voltage applied to the working electrode may be designed to be applied for a long hold, then removed for a brief pause, then reapplied. The integrated current may be measured against the length of the pause to determine ion concentration, as the background ion concentration is reversible, whereas the dilute analyte of interest is not.

To summarise, the concentration of ions in solution may therefore be determined by applying potential to the working electrode, removing or reducing the potential for a pause, reapplying or increasing the potential to the working electrode, and determining the integrated current over the length of the pause.

Alternatively, specific ions could be collected in a separate concentrated waste stream, and the concentration could be analysed with another device.

The method may comprise the additional step of lowering or removing the potential applied between the electrodes to release ions bound to the electrode. Optionally, the ions are released following transfer of the electrodes to a different solution. This enables the collection of environmentally hazardous ions or ions of economic value. On a larger scale, this ability to capacitively adsorb selectively and then discharge specific ions into solution allows for the sequestration and separation of economically valuable ions from mixed ion solutions of low economic value. The SCIDAR electrode technology therefore has enormous scope beyond that of conventional ISEs, representing a significant innovation compared to the state of the art.

The method of the invention may occur as a batch reaction in which the SCIDAR electrode is exposed to a given volume of solution.

Alternatively, the method of the invention may occur as a flow reaction. A peristaltic pump may be provided to pump a solution from a reservoir containing the solution through the capacitive deionisation cell and in between the electrodes of the cell. A current collector may optionally be connected to the electrodes and potentiostat or galvanostat of the cell. After flowing through the cell, the solution may be transported to a separate reservoir or it may be transported back to the source reservoir.

The CDI cell may comprise a holder for the electrodes to hold them in place and keep that at a consistent distance from one another. The holder may be 3D printed. Figure 3 shows CAD software designs of a simple capacitive deionisation cell where; a) shows the well and lid which can be clamped together. The lid has openings for the electrodes to be inserted; b) shows the electrode holders; and c) represents how the electrode holders slot into the well. Ultimately, this design allows for quick and easy access to the electrodes as well as fixing the electrode faces into a set position with repeatable separation, enabling repeatable measurements of capacitive deionisation to be achieved. This is a critical variable with CDI flow cells and optimising the electrodes to a given separation will affect capacitive performance.

The CDI cell of the invention may comprise a wireless communication unit capable of communicating electrochemical readings from the potentiostat and/or conductivity meter to a receiving unit. The receiving unit may be a computer or mobile phone. Thus, the system may be enable remote real time detection of environmental pollutants from effluent plants and water courses. Therefore, surrounding sites could be facilitated at a large scale, providing, in connection with geographical data, real time distributed imaging of aqueous ion pollution, including evolving spillages or other inadvertent releases.

The SCIDAR electrodes of the invention are formed of a conductive material with a high surface area. Preferably, the SCIDAR electrodes are formed of a conductive carbon network selected from graphene, carbon nanotubes, or mixtures thereof. Preferably, the carbon network is formed of a mixture of graphene and carbon nanotubes. The graphene may be cross-linked, for example, via an ester bond.

The term carbon nanotubes refers to nano-scale tubes made substantially of carbon atoms, having a structure based on graphite basal planes that are wrapped or curled to become a tube. Carbon nanotubes have an intrinsically high aspect ratio and nanoscale diameter. Individually, they have high strength, high modulus, useful electrical conductivity, and large surface area. The high surface area and accessible pores provided by carbon nanotubes provides various advantages when used in CDI cells. It enables ions to transport through the electrode rapidly and it provides a high number of convex surfaces which maximises ion accumulation. Furthermore, the nanotube network is highly conductive.

The definition of carbon nanotube encompasses carbon nanotubes of any type, including common carbon nanotubes, variants of common carbon nanotubes, and carbon nanotubes with various modifications. Preferably, the carbon nanotubes exhibit a high conductivity. The term may encompass structures that are not pure carbon, such as those doped with nitrogen or boron, or functionalised with surface groups such as those containing oxygen, hydrogen, or other derivatives. Carbon nanotubes may further be submicron fibres with primarily graphitic (sp^2) or amorphous carbon structures arranged in any crystallographic orientation such as platelet nanofibres and bamboo nanofibres. Preferably, the present invention uses common carbon nanotubes in which the carbon atoms are ideally sp^2 bonded into a graphene-like sheet with cylindrical geometry. Suitable nanotubes may be those that are commercially available such as the products of Applied Sciences Inc., Bayer Chemicals, Cheaptubes Inc., Chengdu Organic Chemicals, Future Carbon, Nanocyl S. A., Nanoshel, Arry International Group Limited, Carbon Nano Materials R&D Center, Carbon Solutions Inc., NanocarbLab (NCL), Nanocs, Thomas Swan Ltd.

Moreover, for the purposes of the present invention, carbon nanotubes may be single-walled carbon nanotubes, double-walled carbon nanotubes or multi-walled carbon nanotubes having more than two layers. Preferably, the nanotubes used in the present invention are single walled or double walled.

Preferably, the carbon nanotubes that may be used in the present invention have a diameter range of from about 0.2 to 10 nm, preferably from about 0.5 to 5 nm, more preferably about 1 to 2 nm. The small diameters of the carbon nanotubes result in a high surface area, which is particularly beneficial for maximising the adsorbance of ions in the context of the present invention. Another notable benefit is that carbon nanotubes with small diameters generally have a higher perfection and so exhibit excellent electrical conductivity.

Preferably, the carbon nanotubes that may be used in the present invention have a length of from about 0.05 to 1000 µm, preferably from about 0.1 to 30 µm, most preferably in the range of about 0.1 to 10 µm.

Preferably, greater than 75 wt% of the nanotubes in the network have dimensions in the ranges set out immediately above.

The carbon nanotubes that may be used in accordance with the present invention may be formed by reaction with a linking molecule comprising at least two functional sites capable of reacting with the surface of said carbon nanotubes, to form a covalently cross-linked gel network. This method is further detailed in European patent number EP2665552B1.

The carbon network may take the form of a film, aerogel or xerogel. Preferably, the carbon network takes the form of an aerogel or a xerogel, most preferably a xerogel. These are highly porous materials with a particularly low envelope density and high surface area. They typically also display exceptional electrical conductivity and robustness. These features are particularly useful for the SCIDAR electrodes of the present invention. Carbon hydrogels may be obtained from pyrolysis of resorcinol-formaldehyde resin.

As used herein, the term "aerogel" refers to a highly porous material of low density, which is prepared by forming a gel and then removing liquid from the gel while substantially retaining the gel structure. Preferably, an "aerogel" according to the present invention comprises a carbon nanotube network wherein the volume change on drying of the gel is less than 30%, preferably less than 20%, preferably less than 10%, preferably less than 5%. Aerogels have open-celled microporous or mesoporous structures. Typically, they have pore sizes of less than 1000 nm and surface areas of greater than 100 m^2 per gram. Preferably, they have pore sizes of less than 200 nm and surface areas of greater than 400 m^2 per gram. They often have low densities, e.g., from 500 mg/cm^3 down to as little as 1 mg/cm^3, preferably in the range of 15 to 300 mg/cm^3 . Exceptionally, unlike other existing aerogels, those produced from high aspect ratio nanotubes, may have low densities, high surface areas, but large pore sizes; in principle, the pore size may approach the scale of the individual nanotube lengths which can reach millimetres or even centimetres.

Preferably, aerogels are materials in which the liquid has been removed from the gel under supercritical conditions, such as supercritical drying or lyophilisation.

The pores in the aerogels used in the present invention are typically filled with air. They can also be filled with other desired gases. Alternatively, the gases can be removed from the aerogel under vacuum.

The term "xerogel" as used herein refers to a type of aerogel in which the volume change on drying of the gel is greater than approximately 30%. The gel may partially collapse during drying, however, the strong covalent network of nanotubes limits the process, yielding a more useful, more porous, less dense structure, than obtained from drying physical gels or other nanotube suspensions. In the present case specifically, the functionalisation can cross link the gel and mitigate the need for drying altogether. The cross-linking avoids re-bundling of the carbon network, and therefore retains a large active surface area.

Preferably, the aerogel or xerogel has a density of from 1 to 1500 mg/cm^3, preferably 200 mg/cm^3 to 1000 mg/cm^3. The aerogel or xerogel may be in the form of a continuously-connected homogenous network.

It is desirable that the resultant carbon nanotube networks contain as few impurities as possible. Such impurities include residual reagents (e.g. coupling agents), surfactants, additives, polymer binders and the like. The presence of these impurities can lead to an increase in the density of the carbon nanotube networks as well as reducing the electrical conductivity and surface area of the carbon nanotube aerogel. Furthermore, the presence of impurities may also introduce unwanted redox signals. This term, however, does not encompass any modification groups, particles or layers such as molecules with ion specific binding sites that have been deliberately added to the carbon nanotube network.

In a preferred embodiment, the electrode is formed of an aerogel network based around carbon nanotubes with an aspect ratio of between 100 and 10000, preferably with aspect ratio of between 200 and 7000. By aspect ratio is meant the ratio between the length and diameter of the carbon nanotubes. Typically, carbon nanotubes have a high aspect ratio since the length of carbon nanotubes is typically in the order of 0.1-100 µm.

The conductive carbon nanotubes that may be used in the present invention have a high electric conductivity of more than 300 S/cm, preferably more than 500 S/cm. Additionally, they allow a current flow at a current density of greater than 10 MA/cm^2, preferably greater than 100 MA/cm^2 or more. A network of carbon nanotubes therefore displays excellent electrical conductivity and current density, compared to other carbon aerogels.

In addition, carbon nanotubes have desirable intrinsic mechanical characteristics, including high strength, stiffness, and flexibility, at low density.

The working SCIDAR electrode or electrodes of the invention are functionalised with ion specific binding sites. This enables the electrode or electrodes to selectively store particular ions following the application of potential across the electrodes in a CDI cell.

The ion specific binding sites may be specific to NO_3^- ions, Au^{3+} ions, Ni^{2+} ions, AsO_3^{3-} ions, AsO_4^{3-} ions, Ag^+ ions, Pt^{2+} ions, Cu^{2+} ions, Pd^{2+} ions, Pb^{2+} ions, Zn^{2+} ions, Mn^{2+} ions, CrO_4^{2-} ions, $Cr_2O_7^{2-}$ ions, Fe^{2+} ions, Fe^{3+} ions, Sn^{2+} ions, Al^{3+} ions, In^{3+} ions, Cd^{2+} ions, Co^{2+} ions, Hg^{2+} ions, K^+ ions, Mg^{2+} ions, Na^+ ions, or combinations thereof. Preferably, the ion specific surfaces are specific to NO_3^- ions, Au^{3+} ions, Ni^{2+} ions, AsO_3^{3-} ions or combinations thereof.

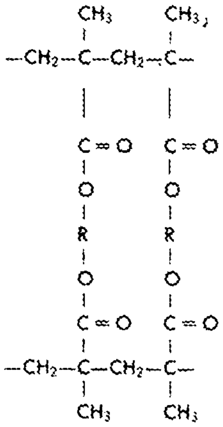
The working electrode may be surface functionalised with ion specific binding sites. Alternatively, the working electrode may be a host matrix to ion specific binding sites. For example, the working electrode may host particles such as nanoparticles that are capable of coordinating to specific ions. In the case of a working electrode formed of a conductive carbon network, the particles may be held in place between graphene sheets.

The ion specific binding sites range from discrete, individual coordination sites to continuous polymer layers. The ion specific binding sites may be resins, chelants, polymers, oxy rings, macrocyles or combinations thereof. Preferably, the ion specific binding site is formed of a polymer layer.

Examples of suitable molecules with ion specific binding sites include: polyvinyl ferrocene, 1-dodecylbenzene; ion exchange resins such as polymethacrylate resins, Amberlite XAD-7, Bonlite BA304, polystyrene crosslinked with divinylbenzene or Purolite A-500; chitin, crab shells avid washed and heat treated in the absence of oxygen, redox active polymers such as polyhydroquinone (PHQ), polytyramine (PTA), poly(meta-aminophenol (PmAP), poly(para-phenylenediamine) (PpPDA); SDS modified with 3-(4-chlorobenzylideneamino)-2-thioxthiazolodin-4-one, polyethylenimine (PEI)-grafted gelatine sponge, Fe(III)/Cr(III) hydroxide, hydrated ferric oxide particles, Cu^{2+} loaded chelating resins such as DOW 2N or DOW 3N.

Molecules with binding sites specific to Au ions include: PHQ, PTA, PmAP, PpPDA, ion exchange resins such as Amberlite XAD 7, Bonlite B1304, Purolite A-500 and chitin. PpPDA in particular was shown to extract 99.9% of Au in complex water sources when deposited on a metal organic framework (MOF). The extraction demonstrated minimal update of competitor ions due to secondary and tertiary amine groups. Efficient extraction of Au^{3+} was shown across all pH levels from pH2 to pH 11 [3].

Amberlite XAD-7 has the following structure:



Molecules with binding sites specific to As ions include: PVF, Cu^{2+} loaded chelating resins DOW 2N and DOW 3N; and hydrated ferric oxide particles.

Molecules with binding sites specific to Cd^{2+} ions include: SDS modified with 3-(4-chlorobenzylideneamino)-2-thioxothiaazolodin-4-one, PEI-grafted gelatine sponge and Fe(III)/Cr(III) hydroxide.

Preferably, the working electrode, which may be a carbon network, is functionalised with ion specific binding sites by direct chemical methods. For example, the conductive material forming the working electrode may be mixed and coated with a polymer.

Another direct chemical functionalisation method involves reacting the surface of the working electrode. For example, when the working electrode is formed of a conductive carbon network, the carbon network may be reduced to form a charged carbon network prior to surface functionalisation. Preferably, the charged carbon network is selected from nanotubide or graphenide.

The carbon network, or charged carbon network may be functionalised through an electrochemical reaction with diazonium.

Molecules with ion specific binding sites may be added to the conductive material forming working electrode during the formation of the working electrode, after the formation of the working electrode, or both.

The potential applied to the CDI electrodes of the invention may be optimised to maximise adsorption of specific ions and minimise the adsorption of potential interference ions.

For ion concentrations below the detection limits of a single SCIDAR electrode, two or more ion detection devices can be coupled, such that the output of the first device passes concentrated ions into a second detection device, via an automated sampling process. The pre-concentration device selectively collects the desired ions from a large volume of feed water, then discharges the ions into the second device, for example, at an order of magnitude higher concentration. The process can be repeated as necessary to increase the required sensitivity. Hence, the SCIDARs can access concentration regimes below its initial limits of detection. This is something that ISE's cannot achieve.

The solution is preferably aqueous. More preferably, the solution is brackish water or sea water. The solution preferably has some background electrolyte concentration.

In a second aspect, the invention provides a device for detecting ion concentration in a solution comprising a working electrode. The working electrode comprises a carbon nanotube network formed of an aerogel or a xerogel, as discussed above. The carbon nanotube network is functionalized with ion specific binding sites.

Preferably, the device is a capacitive deionisation cell. The device may have one carbon nanotube electrode, or may have two or more. Preferably, there is one carbon nanotube working electrode.

In a preferred embodiment, the device comprises one or more of a power supply, a potentiostat and a charge collector. The device may also comprise a means for determining the charging current and a means for determining the voltage.

The ion specific binding sites of the electrodes are preferably specific to those ions listed above.

Preferably, the carbon nanotubes of the electrode are single walled carbon nanotubes.

The aerogel or xerogel preferably has a density of from 1 to 1500 mg/cm^3. The aerogel or xerogel is preferably in the form of a continuously-connected homogeneous network.

The carbon nanotube network may be functionalised with ion specific binding sites through surface functionalisation. Alternatively, the carbon nanotube network is coated with a polymer with ion specific binding sites.

The ion specific binding sites may be resins, polymers, oxy rings, macrocycles or combinations thereof. They may be derived from the molecules listed above.

The device may have a peristaltic pump capable of pumping a solution between the electrodes. This enables a flow reaction set up.

The device may comprise a holder for the capacitive deionisation cell, which is capable of holding the electrons in place. The holder may also hold the charge collector in place. In some examples, the holder may be 3D printed.

Preferably, the device comprises a wireless communication unit, enabling the communication of conductivity and/or ionic concentration readings to a receiving unit such as a computer or mobile phone. This enables the remote control of the device and monitoring of the outputs of the device.

In a third aspect, the invention provides a system for detecting an ion concentration in a solution. The system comprises a reservoir comprising the solution, a capacitive deionisation cell comprising a working electrode, a reference electrode and a power supply, wherein the working electrode is formed of a high surface area conductive material functionalised with ion specific binding sites, as described herein. A means is also provided for determining the capacitive charging current and voltage on the working electrode following application of potential across the working electrode in the solution.Preferably the high surface area conductive material is a conductive carbon network.

All cited art is incorporated in its entirety by reference.

REFERENCES

[1] Flanagan S et al., *Arsenic in tube well water in Bangladesh: health and economic impacts and implications for arsenic mitigation*, Bull World Health Organ, 2016. **90**: pp. 839–846

[2] Myagkaya, I.N. et al., *Gold and silver in a system of sulfide tailings. Part 1: Migration in water flow.* Journal of Geochemical Exploration, 2016. **160**: p. 16-30.

[3] Sun, D.T., et al., *Rapid, Selective Extraction of Trace Amounts of Gold from Complex Water Mixtures with a Metal-Organic Framework (MOF)/Polymer Composite.* J Am Chem Soc, 2018. **140**(48): p. 16697-16703.

CLAIMS

1. A method for detecting the concentration of an ion in a solution, wherein the method comprises the steps of:

a) providing a capacitive deionisation cell comprising a working electrode, wherein the working electrode is formed of a high surface area conductive material and wherein the high surface area conductive material is functionalised with ion specific binding sites;

b) providing a means for determining the capacitive charging current and voltage on the working electrode;

c) determining the concentration of ions in the solution from the changes in the charging current and voltage over time following application of potential across the working electrode in the solution.

2. The method according to claim 1, wherein the high surface area conductive material is a conductive carbon network.

3. The method according to any preceding claim, wherein the ion specific binding sites are specific to NO_3^- ions, Au^{3+} ions, Ni^{2+} ions, AsO_3^{3-} ions, AsO_4^{3-} ions, Ag^+ ions, Pt^{2+} ions, Cu^{2+} ions, Pd^{2+} ions, Pb^{2+} ions, Zn^{2+} ions, Mn^{2+} ions, CrO_4^{2-} ions, $Cr_2O_7^{2-}$ ions, Fe^{2+} ions, Fe^{3+} ions, Sn^{2+} ions, Al^{3+} ions, In^{3+} ions, Cd^{2+} ions, Co^{2+} ions, Hg^{2+} ions, K^+ ions, Mg^{2+} ions, Na^+ ions, or combinations thereof.

4. The method according to claim 3, wherein the ion specific binding sites are specific to NO_3^- ions, Au^{3+} ions, Ni^{2+} ions, AsO_3^{3-} ions or combinations thereof.

5. The method according to any one of claims 2-4, wherein the carbon network is formed of graphene, carbon nanotubes or mixtures thereof.

6. The method according to claim 5, wherein the carbon network is formed of graphene and wherein the graphene is cross-linked.

7. The method according to claim 6, wherein said graphene is cross-linked via an ester bond.

8. The method according to claim 5, wherein the carbon network is formed of carbon nanotubes, wherein the carbon nanotubes are single-walled carbon nanotubes, double-walled carbon nanotubes or multi-walled carbon nanotubes.

9. The method according to claim 8, wherein the carbon nanotubes are single-walled carbon nanotubes.

10. The method according to any preceding claim, wherein the carbon network is a film, aerogel, xerogel or mixtures thereof.

11. The method according to claim 10, wherein said aerogel or xerogel has a density of from 1 to 1500 mg/cm^3.

12. The method according to claim 10 or claim 11, wherein said aerogel or xerogel is in the form of a continuously-connected homogeneous network.

13. The method according to any preceding claim, wherein the high surface area conductive material is surface functionalised with ion specific binding sites.

14. The method according to any preceding claim, wherein the high surface area conductive material is coated with a polymer with ion specific binding sites.

15. The method according to claim 13, wherein the high surface area conductive material is formed of a carbon network, wherein the carbon network is reduced to form a charged carbon network prior to surface functionalisation, preferably wherein the charged carbon network is selected from nanotubide or graphenide.

16. The method according to claim 13, wherein the high surface area conductive material is formed of a carbon network, wherein the carbon network is functionalised through an electrochemical reaction with diazonium

17. The method according to any preceding claim, wherein the ion specific binding sites are resins, chelants, polymers, oxy rings, macrocycles or combinations thereof.

18. The method according to any preceding claim, wherein the ion specific binding site is derived from polyvinyl ferrocene 1-dodecylbenzene; ion exchange resins such as polymethacrylate resins, Amberlite XAD-7, Bonlite BA304, polystyrene crosslinked with divinylbenzene or Purolite A-500; chitin, crab shells avid washed and heat treated in the absence of oxygen, redox active polymers such as polyhydroquinone (PHQ), polytyramine (PTA), poly(meta-aminophenol (PmAP), poly(para-phenylenediamine) (PpPDA); SDS modified with 3-(4-chlorobenzylideneamino)-2-thioxthiazolodin-4-one, polyethylenimine (PEI)-grafted gelatine sponge, Fe(III)/Cr(III) hydroxide, hydrafted ferric oxide particles, Cu^{2+} loaded chelating resins such as DOW 2N or DOW 3N.

19. The method according to any preceding claim wherein the capacitive deionisation cell comprises a counter electrode.

20. The method according to claim 19, wherein the capacitive charging current is measured across the working electrode and the counter electrode.

21. The method according to claim 19, wherein the capacitive deionisation cell comprises a reference electrode.

22. The method according to claim 21, wherein the capacitive charging current is measured on the working electrode.

23. The method according to any preceding claim further comprising the step of lowering the potential applied to the working electrode to release ions bound to the electrode.

24. The method according to claim 23, wherein the ions are released following transfer of the electrodes to a separate waste solution.

25. The method according to any preceding claim, wherein the solution flows through the capacitive deionisation cell.

26. The method according to claim 25, further wherein the capacitive deionisation cell further comprises a peristaltic pump to pump the solution between the electrodes.

27. The method according to any preceding claim, wherein the capacitive deionisation cell comprises a holder for the electrodes.

28. The method according to claim 27, wherein the holder is 3D printed.

29. The method according to any preceding claim, wherein the solution is aqueous, preferably wherein the solution is brackish water or sea water.

30. The method according to any preceding claim, wherein the ion selectivity of the working electrode is pre-determined.

31. The method according to claim 30, wherein the concentration of ions in solution is determined by

comparing the capacitance of the functionalised working electrode to the capacitance of an unfunctionalized reference device; and

comparing this difference in capacitance to the pre-determined selectivity of the working electrode

32. The method according to claim 23, wherein the concentration of ions in solution is determined by

removing or reducing the potential applied to the working electrode for a pause;

reapplying or increasing the potential to the working electrode; and

determining the integrated current over the length of the pause.

33. The method according to claim 24, wherein the concentration of ions in solution is determined by a separate capacitive deionisation cell in the waste solution comprising the released ions.

34. A device for detecting ion concentration in a solution comprising a working electrode; wherein the working electrode comprises a carbon nanotube network, wherein the carbon nanotube network is an aerogel or xerogel and wherein the carbon nanotube network is functionalised with ion specific binding sites.

35. The device according to claim 34, wherein the device is a capacitive deionisation cell.

36. The device according to any one of claims 34-35, wherein the device comprises one or more of: a power supply, a potentiostat, a galvanostat and a charge collector.

37. The device according to any one of claims 34-36, wherein the ion specific surfaces are specific to NO_3^- ions, Au^{3+} ions, Ni^{2+} ions, AsO_3^{3-} ions, $As^5O_4^{3-}$ ions, Ag^+ ions, Pt^{2+} ions, Cu^{2+} ions, Pd^{2+} ions, Pb^{2+} ions, Zn^{2+} ions, Mn^{2+} ions, CrO_4^{2-} ions, $Cr_2O_7^{2-}$ ions, Fe^{2+} ions, Fe^{3+} ions, Sn^{2+} ions, Al^{3+} ions, In^{3+} ions, Cd^{2+} ions, Co^{2+} ions, Hg^{2+} ions, K^+ ions, Mg^{2+} ions, Na^+ ions, or combinations thereof.

38. The device according to claim 37, wherein the ion specific surfaces are specific to NO_3^- ions, Au^{3+} ions, Ni^{2+} ions, As^{3+} ions or combinations thereof.

39. The device according to any of claims 34-38, wherein the carbon nanotubes are single-walled carbon nanotubes, double-walled carbon nanotubes or multi-walled carbon nanotubes.

40. The device according to any one of claims 34-39, wherein said aerogel or xerogel has a density of from 1 to 1500 mg/cm^3.

41. The device according to any one of claims 34-40, wherein said aerogel or xerogel is in the form of a continuously-connected homogeneous network.

42. The device according to any one of claims 34-41, wherein the carbon network is surface functionalised with ion specific binding sites.

43. The device according to any one of claims 34-42, wherein the ion specific binding sites are resins, polymers, oxy rings, macrocycles or combinations thereof.

44. The device according to any one of claims 34-43, wherein the ion specific binding site is derived from polyvinyl ferrocene 1-dodecylbenzene; ion exchange resins such as polymethacrylate resins, Amberlite XAD-7, Bonlite BA304, polystyrene crosslinked with divinylbenzene or Purolite A-500; chitin, crab shells avid washed and heat treated in the absence of oxygen, redox active polymers such as polyhydroquinone (PHQ), polytyramine (PTA), poly(meta-aminophenol (PmAP), poly(para-phenylenediamine) (PpPDA); SDS modified with 3-(4-chlorobenzylideneamino)-2-thioxthiazolodin-4-one, polyethylenimine (PEI)-grafted gelatine sponge, Fe(III)/Cr(III) hydroxide, hydrafted ferric oxide particles, Cu2+ loaded chelating resins such as DOW 2N or DOW 3N

45. The device according to any one of claims 34-44, further comprising a peristaltic pump capable of pumping a solution between the electrodes.

46. A system for detecting an ion concentration in a solution comprising:

a reservoir comprising the solution;

a capacitive deionisation cell comprising a working electrode and a power supply, wherein the working electrode is formed of a high surface area conductive material and wherein the high surface area conductive material is functionalised with ion specific binding sites; and

a means for determining the capacitive charging current and voltage on the working electrode following application of potential across the working electrode in the solution.

47. The system according to claim 46, wherein the high surface area conductive material is a conductive carbon network.

Figure 1

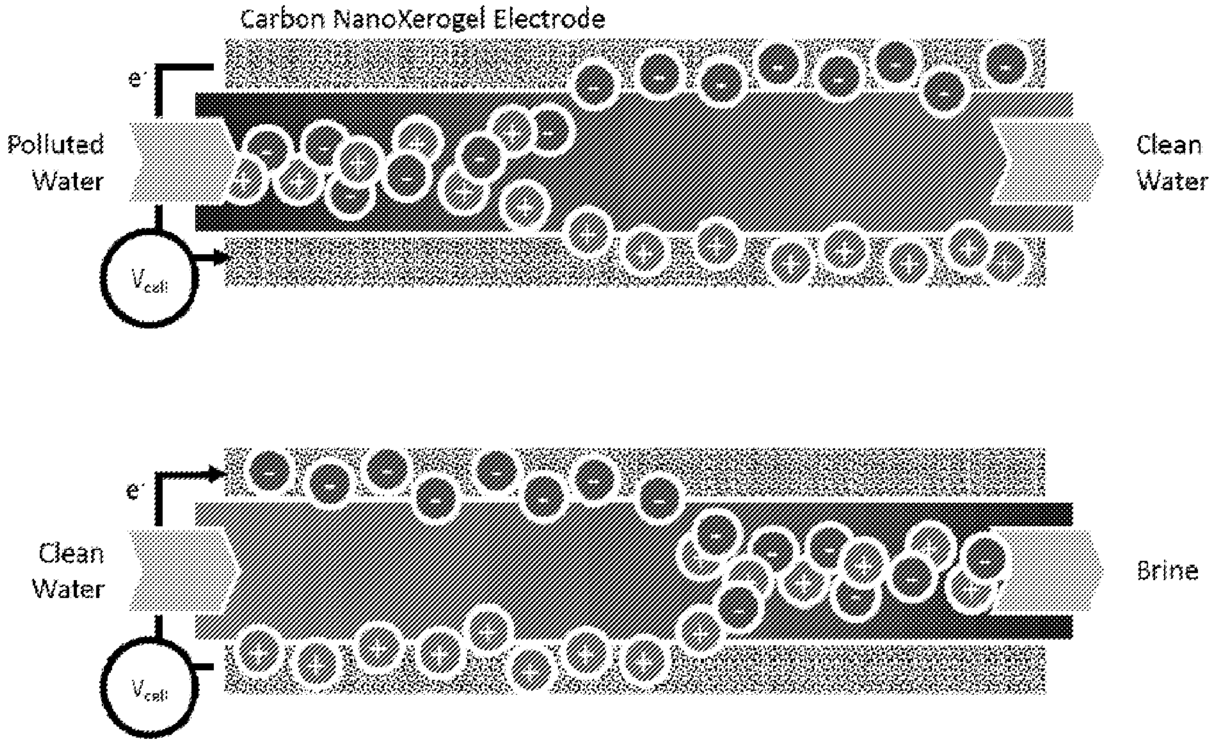

Carbon NanoXerogel Electrode
e⁻
Polluted Water
Clean Water
V_{cell}
e⁻
Clean Water
Brine
V_{cell}

Figure 2

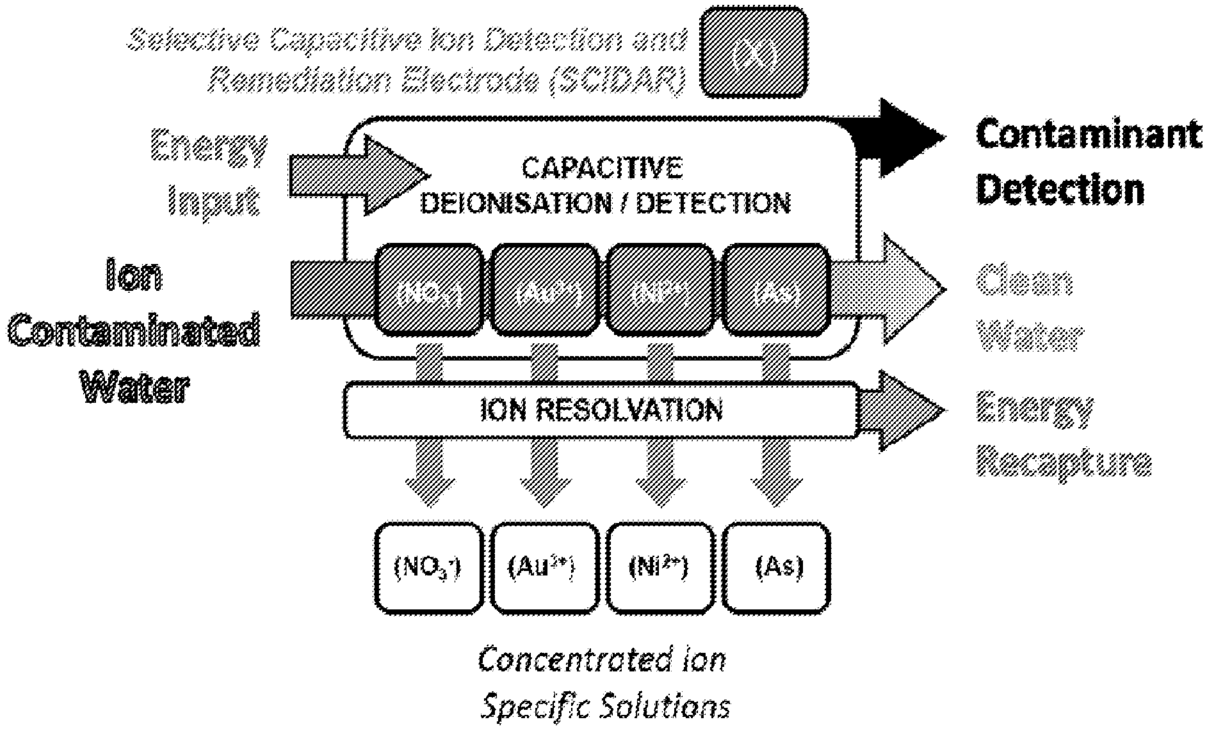
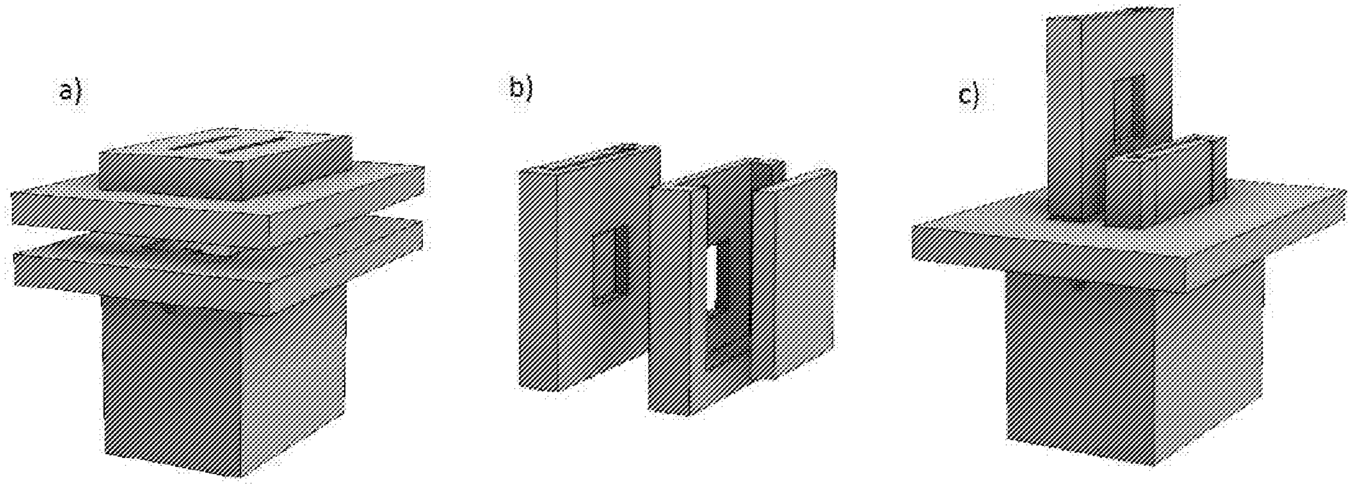

Selective Capacitive Ion Detection and Remediation Electrode (SCIDAR)
(X)
Energy Input
Ion Contaminated Water
CAPACITIVE DEIONISATION / DETECTION
(NO_3^-)
(Au^{3+})
(Ni^{2+})
(As)
Contaminant Detection
Clean Water
ION RESOLVATION
Energy Recapture
(NO_3^-)
(Au^{3+})
(Ni^{2+})
(As)
Concentrated Ion Specific Solutions

Figure 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2020/053209

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N27/42 G01N33/18 C02F1/469
ADD. G01N27/30

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)
G01N C02F

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	Chadwick Nicholas P ET AL: "Rapid Detection of High Value Pollutants 'DetectION'", ATTRACT final conference, 22 September 2020 (2020-09-22), pages 1-5, XP055832166, Retrieved from the Internet: URL:https://phase1.attract-eu.com/wp-content/uploads/2019/05/DetectION.pdf [retrieved on 2021-08-16]	1-5, 8-15,17, 19-47
Y	the whole document ----- -/--	5-7,16

☒ Further documents are listed in the continuation of Box C.

☐ 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

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"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 17 August 2021	Date of mailing of the international search report 27/08/2021
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 Klein, Marc-Oliver

2

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ZHANG MENG ET AL: "Recent progress in graphene-based and ion-intercalation electrode materials for capacitive deionization", JOURNAL OF ELECTROANALYTICAL CHEMISTRY, ELSEVIER, AMSTERDAM, NL, vol. 878, 22 September 2020 (2020-09-22), XP086362966, ISSN: 1572-6657, DOI: 10.1016/J.JELECHEM.2020.114703 [retrieved on 2020-09-22] the whole document -----	1-47
X	KIM YU-JIN ET AL: "Selective removal of nitrate ion using a novel composite carbon electrode in capacitive deionization", WATER RESEARCH, vol. 46, no. 18, 31 August 2012 (2012-08-31), pages 6033-6039, XP028944395, ISSN: 0043-1354, DOI: 10.1016/J.WATRES.2012.08.031 fig. 3,4 and corresponding text passages abstract -----	1-4,13, 14, 17-20, 22-27, 29-31, 34-38, 43-47
A	IZAAK COHEN ET AL: "Bromide Ions Specific Removal and Recovery by Electrochemical Desalination", ENVIRONMENTAL SCIENCE & TECHNOLOGY, vol. 52, no. 11, 11 May 2018 (2018-05-11), pages 6275-6281, XP055618821, US ISSN: 0013-936X, DOI: 10.1021/acs.est.8b00282 the whole document -----	1-47
Y	SHI WENHUI ET AL: "Ultrahigh Performance of Novel Capacitive Deionization Electrodes based on A Three-Dimensional Graphene Architecture with Nanopores", SCIENTIFIC REPORTS, vol. 6, no. 1, 5 January 2016 (2016-01-05), pages 1-9, XP055832180, abstract fig. 5 and corresponding text passages, especially p. 6, l. 8 where the integration of the current is discussed for the electrosorption capacity which equals the concentration of the bound ions of the solution. -----	5-7

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AHMED MD ASHIQUE ET AL: "Capacitive deionization: Processes, materials and state of the technology", JOURNAL OF ELECTROANALYTICAL CHEMISTRY, ELSEVIER, AMSTERDAM, NL, vol. 813, 16 February 2018 (2018-02-16), pages 178-192, XP085360925, ISSN: 1572-6657, DOI: 10.1016/J.JELECHEM.2018.02.024 the whole document -----	1-47
Y	PAN XIAORU ET AL: "Research progress of graphene-based nanomaterials for the environmental remediation", CHINESE CHEMICAL LETTERS, ELSEVIER, AMSTERDAM, NL, vol. 31, no. 6, 12 October 2019 (2019-10-12), pages 1462-1473, XP086205138, ISSN: 1001-8417, DOI: 10.1016/J.CCLET.2019.10.002 [retrieved on 2019-10-12] p. 1469, right column, first par. -----	16

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