Rapid Detection of High Value Pollutants 'DetectION'

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ABSTRACT

Ion pollution in water causes a wide range of environmental and health problems across the world, including throughout Europe. The extent of the problem is growing, and there is, therefore, an urgent need to develop practical strategies to mitigate this. In this project, we develop a new system to detect and ultimately collect aqueous ion pollution using capacitive deionisation (CDI). Selective capacitive ion detection and remediation (SCIDAR) electrodes leverage established ion specific surfaces and applies them within state-of-the-art nanocarbon aerogels. This strategy provides robust ion detection mechanisms based on capacitance measurements and the ability to concentrate ions from solution via CDI. The project has a wider vision to convert waste aqueous ions into a high value commodity which will facilitate the emergence of circular economies and provide resources to promote the implementation of this clean-up technology.

Keywords: capacitive deionisation; ion pollution; aerogels; SCIDAR.

1. INTRODUCTION

Water contaminated with ions from sources such as heavy metals and fertilisers causes a wide range of environmental and health problems around the world. As one example, over 140m people in 70 countries drink water contaminated with arsenic (As), a known carcinogen, leading directly to the deaths of over 40,000 Bangladeshis each year [1]. Other aqueous ionic pollutants have potential economic value; these include precious metals such as gold (Au) found in mine waste streams and "tailings". Detection and removal of such precious metals and other ions of economic importance will lead to waste stream value creation and facilitate emergence of circular economies, which has been promoted by the UN as part of the strategy to meet the Sustainable Development Goals (SDGs) [2].

Capacitive deionization (CDI) is a technique for removing dissolved ions from aqueous solutions, typically by applying an electrical field between a pair of porous electrodes with a separator in-between (Fig.1). The separator in this case is the aqueous solution and the electrode material used typically includes activated carbon, graphene, carbon nanotubes and carbon aerogels due to their intrinsic low resistivity and high surface area [3-5]. The high surface area of the porous electrodes increases the charge storage capacity of capacitive electrochemical cells. Similar to double-layer (DL) supercapacitors which store electrons, capacitive deionization cells store ions [6].

The primary objective of this project was to create ion selective CDI electrodes for the rapid inline detection, sensing and sequestration of ion pollutants in water down to commercially relevant concentration levels. Whilst this new technology is, in principle, generally applicable, we have selected the following ions for initial development: gold (Au_{3+}) and arsenic (As_{3+}/As_{5+}). These examples have particularly significant economic potential or environmental need in detection and remediation. We have designed the 'DetectION' concept with a strong focus on deriving direct economic value from ion pollutant detection, something which is not commonplace industrially. The project is focused on developing a new mechanism for ion detection, which integrates the possibility for ion collection. Selective Capacitive Ion Detection and Remediation (SCIDAR) electrodes leverage established ion specific surfaces and applies them within state-of-the-art nanocarbon aerogels. This strategy provides robust ion detection mechanisms based on capacitance measurements and the ability to concentrate ions from solution via capacitive deionisation. Patent protected nanocarbon aerogel networks provide the high surface area, conductivity, and hierarchical structure required for maximising the signal and concentration efficiencies.

2. STATE OF THE ART

The current state of the art for ion detection in solution is through Ion Selective Electrodes (ISE's). Ion selective electrodes rely on the small potential differences arising

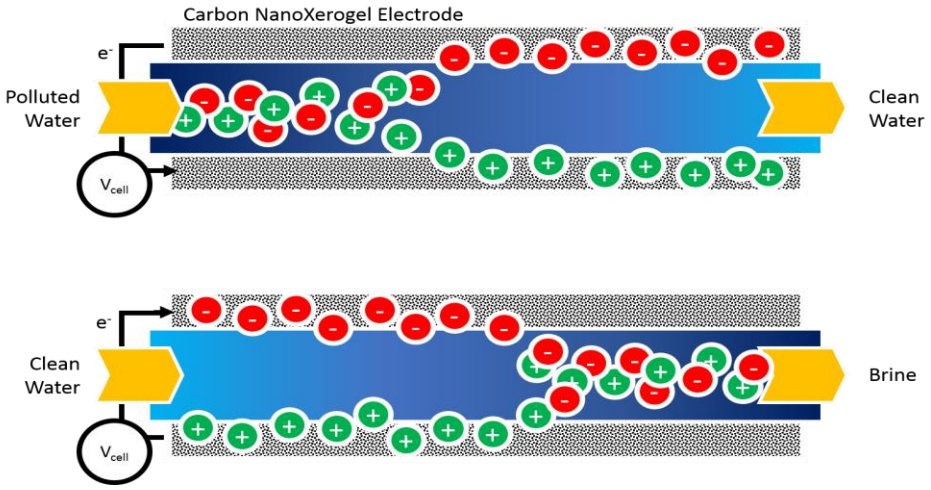

Fig. 1. Schematic showing the operation of a CDI cell in polluted water. Upon charging of the cell ions are drawn electrostatically to electrodes of opposite charge. Once the charge is released the ions are released. By holding the cell in a charged state, ions are separated from water realising cleaner water.

between the target solution and a reference solution. These devices, however, exhibit operational issues for long term, remote usage. In particular, they experience 'calibration drift' that results in inaccurate readings, and generally require daily recalibration. We will circumvent this issue, by exploiting a different, capacitive, detection mechanism, whilst using the established ion selective surfaces used in ISE's to afford the required selectivity.

3. BREAKTHROUGH CHARACTER OF THE PROJECT

The project is based around a new mechanism for ion detection, which incorporates the possibility for ion collection. Selective Capacitive Ion Detection and Remediation (SCIDAR) (Fig. 2) electrodes leverage established ion specific surfaces and applies them within state-of-the-art nanocarbon aerogels. This strategy provides robust ion detection mechanisms based on capacitance measurements and the ability to concentrate ions from solution via CDI.

The use of nanocarbon-based aerogels will provide the necessary high surface area, and high conductivity required for efficient capacitive detective, at high speeds, with low loss. Whilst existing ISEs are intrinsically very sensitive, the SCIDAR system has the advantage that it will measure the cumulative capacitive charge developed within the selective aerogel electrodes, rather than relying on an instantaneous electric potential, as developed in ISEs. The timescale of the capacitive measurement can be adjusted to suit different concentration ranges. Once finished the capacitor is

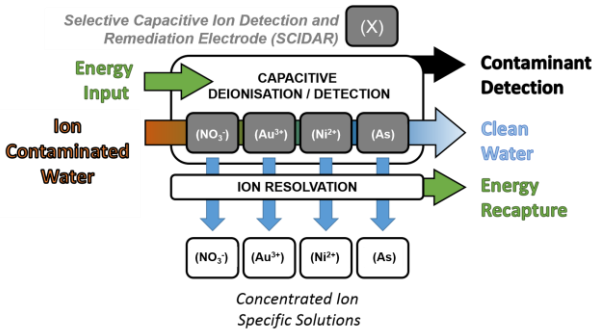

Fig. 2. A schematic showing the overall process of ion pollutant detection using selective capacitive ion detection and remediation (SCIDAR) electrodes. The detection technology also allows for the recovery for the pollutant ions in separate concentrated solutions. Thus there is capacity for the concept to also act as a future environmental remediation technology.

discharged, releasing the ions back into solution and allowing the capacitive sensor to be reused.

For ion concentrations below the detection limits of a single SCIDAR electrode, two (or more) 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 provide the required sensitivity. Hence the SCIDARs can access concentration regimes below its initial limits of detection, something which ISEs cannot achieve. 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 development of SCIDAR technology will initially be applied to detection, but has enormous scope beyond that of conventional ISEs, representing a significant innovation compared to the state of the art.

4. PROJECT RESULTS

Core results involve the initial testing of carbon nano-constructs as a viable route to capacitive deionisation and device development into a suitable flow cell set-up for reliable measurements. To achieve a suitable electrode set-up and to test the electrodes, solvent exchange was required to purge the high porosity of the carbon structures and equilibrate with a solution of H_2O. This multi-step procedure involved careful adjustments to a solvent solution until solvent exchange had occurred.

Electrode analysis was achieved through cyclic voltammetry (CV) and impedance spectroscopy. Typical CV shows that the carbon electrodes are very capacitive in nature, due to their high porosity, and there are no artificial reaction occurring during a CV cycle (Fig. 3.). To achieve repeatable measurements of capacitive deionisation, a cell holder was designed, and 3D printed. Using pre-existing concepts of flow cell technology, a flow through cell was designed to incorporate the carbon electrodes and aluminium charge collectors. This allowed a flow of NaCl (1 gL^{-1}) to pass over the electrodes when a potential is applied (Fig. 4.).

Results also show the charge-discharge cycle of the electrodes when a potential of +1 V is applied over 4200 seconds (Fig. 5.). During this charging process, it can be seen that the current decreases in an exponential function. Interestingly, the conductivity of the solution passing through the flow cell has decreased during the charging process. From an initial conductivity of 1934 µS down to 1747 µS, a decrease of 187 µS.

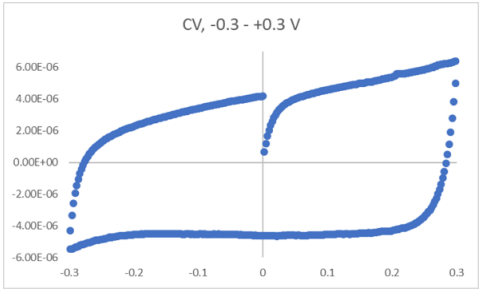

Fig. 3. Cyclic voltammetry of a porous carbon electrode from -0.3 - +0.3 V, in a NaCl solution (1g/L), Ag|AgCl reference electrode.

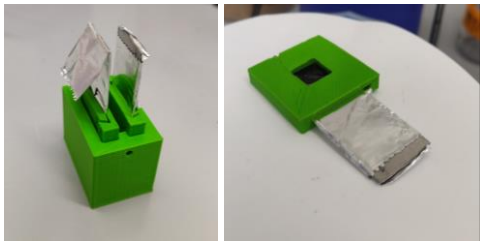

Fig. 4. Photograph showing the 3D printed cell holder consisting of two electrodes spaced a fixed width allowing for solvent to flow through. The carbon electrodes can be submerged with connections though an aluminium charge collector.

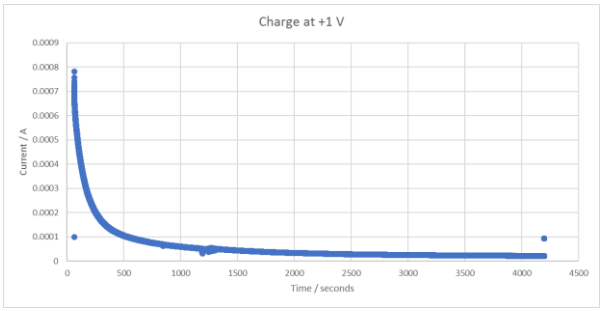

Fig. 5. Charge cycle of a carbon electrode at +1 V for 4200 seconds within the flow cell setup. Electrolyte used was NaCl (1 gL^{-1}).

During the discharge cycle at -1 V, however, some electrolyte appears to have been absorbed into the electrode and not released, apparent through the absence of a conductivity increase when potential was reversed. This could be attributed to the high surface area and porosity of the electrodes. Further investigation into the flow cell setup and electro-absorption of the electrodes will be necessary for demonstrative CDI experiments.

5. FUTURE PROJECT VISION

5.1. Technology Scaling

Scaling the technology from the Technology Readiness Level (TRL) 2 achieved in this ATTRACT Phase 1 project to TRL 5 will involve: i.) demonstration of significant and robust ion removal and release when the potential is applied and removed, respectively; this will inform specifications regarding the level of applied potential and the time required to bind ions (using conductivity measurements) and also methodology for reversing the process and releasing the ions (TRL 3).; ii.) demonstration of ion specificity to select and remove ions of economic (e.g. Au) or environmental (e.g. As)

interest (TRL 4); iii.) demonstration of the concept in its entirety in a well-controlled field trial (TRL 5).

5.2. Project Synergies and Outreach

Expanding the consortium to include additional partners from relevant companies and industries will be critical to realising the vision and building momentum. We would seek out partners who could independently test the concept in their laboratories and provide feedback on its performance and usability. In addition, we will connect with other ATTRACT Phase 1 cohort members to look for opportunities and synergies.

We plan to publicly disseminate results through peer-reviewed articles published in international journals to educate the academic community on the technology. We will keep the public up-to-date on our progress during Phase 2 through a new website which will host webinars, and other interactive sessions. The benefits of the technology will be shared with potential early adopters of the technology at industry-focused conferences

5.3. Technology application and demonstration cases

The SCIDAR technology described here represents a major technological advance on the current state-of-the-art and will have a diverse range of possible applications in areas such as environmental remediation, resource recovery and the establishment of a circular economy. The ability to separate and isolate ions from mixed solutions has the potential to enhance recycling in areas such as electronics. Precious metals such as gold, silver and palladium exist in small amounts in individual consumer electronic devices but represent commercially viable quantities when considering the volume of electronic waste produced annually. For ions which represents a significant health risk to human beings and wildlife, the active and rapid detection of arsenic ions will empower governments to remove this from municipal drinking sources. Furthermore, SCIDAR electrodes could be applied to help geochemists identify low ion concentrations in groundwater and low concentration ion contaminants as well as detect low concentrations of ions in biological fluids such as blood and urine.

While the SCIDAR technology is, in principle, generally applicable, we have selected the following ions for initial development: gold (Au_{3+}), arsenic (As_{3+}/As_{5+}), nitrate (NO_{3-}), and nickel (Ni_{2+}). These specific examples have particularly significant economic potential in detection and/or environmental need of remediation. We have designed the 'DetectION' concept with a strong focus on deriving direct economic value from ion pollutant detection, something which has not been commonplace industrially to date.

Over a ten-year period the successful development of this technology could benefit European society and its economy in the following ways:

- A novel enabling technology enhancing European commercial activity, creating jobs directly in the manufacture and development of the SCIDAR technology and indirectly in its implementation and roll-out,
- A commercial sector extracting value from new sources, including wastewater pollution streams, supporting accelerated implementation of remediation, shifting focus towards circular markets,
- Reductions in industrial and agricultural pollution entering natural water sources through rapid detection and monitoring,
- Reductions in health issues related to industrial pollution, saving money in health expenditure,
- A greater understanding of the effect ion pollution has upon health and the economy,
- New capabilities enabling innovative medical diagnostic technologies.

The SCIDAR technology will benefit the European research community by providing a new 'gold standard' methodology for ion detection and collection in aqueous media, establishing new avenues of research and discovery in disciplines such as environmental science, geochemistry and many related areas.

5.4. Technology commercialization

Commercial applications for such a technology have significant economic potential for established and new industrial technologies. Ion isolation from mixed solutions has the potential to change the value system of aqueous pollution enabling circular economies. Aqueous processing of electronics-related waste, to retrieve gold and silver, would be possible through the 'DetectION' concept using SCIDAR electrodes.

Arsenic detection and removal from municipal sources will also allow governments to save money in the process. A study in the Netherlands estimated that the national government could save €3 million a year per wastewater plant by reducing arsenic to parts per trillion levels. The money saved in public health expenditure would more than pay for the removal of arsenic ions.

In addition, the project will increase and facilitate research in many scientific disciplines related to ion pollution. Opportunities include areas such as

geochemistry, environmental science, chemical engineering and medical technologies.

5.5. Envisioned risks

There are substantial technical risks associated with development of the SCIDAR technology that would need to be addressed in a potential ATTRACT Phase 2 project.

Development of the chemistries for functionalising the SCIDAR electrodes and ensuring selectivity of ion collection might prove more challenging than expected; this risk would be mitigated by building a team with the necessary expertise to ensure the numerous potential chemistries (many already identified) are investigated and assessed.

Comprehensive and selective ion removal in real-world waterways and industrial effluents may prove challenging due to the potential for interference by other ions or compounds or for electrode fouling; this risk would be mitigated by careful laboratory testing to identify potential interfering ions and the use of applied potentials in ranges that preclude such interference.

Travel disruption in Europe will make it more challenging to establish an international consortium, which will be mitigated by taking the opportunity to meet other ATTRACT teams through the network.

5.6. Liaison with Student Teams and Socio-Economic Study

An experienced person will be nominated to facilitate an MSc. level explanation of the projects, and its long-term vision. We would prepare videos and teaching material for online classes, and discussion groups. We would contribute to the socio-economic study of the ATTRACT initiative and ecosystem by providing opportunities for monthly interviews with key personnel in the consortium and by providing case studies on different applications of the virus-laser technology.

6. ACKNOWLEDGEMENT

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