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General Comment

One word. Water. Support methods to decrease cooling tower water use and to save water in general.

See a technology with which to do that here:

https://www.nsf.gov/awardsearch/showAward?AWD_ID=2222557

Attachments

Historical introduction to CDI

Marc Andelman, Mespilus inc, 1 Parkton Ave, Worcester, MA 016050

Motivation

The USGS says that the vast majority of freshwater reserves are ground water[i]. There is much more brackish ground water than fresh ground water[ii]

The most difficult class of contaminants to treat in ground water and recycled water are total dissolved solids (t.d.s.). This includes excess salts, minerals, toxins like nitrate, fluoride, arsenic, and heavy metals. Basic technologies to purify ground water or recycle water are few and have been incrementally improved over a long period of time. It is extremely difficult to invent fundamental, new, and better ways to treat t.d.s. There is at present only one widely used method to remove t.d.s in most situations. That is of course reverse osmosis or RO. This works by pushing water through tight, easily fouled membranes under high pressure. Common forms of t.d.s present in ground water complicate brackish water purification by forming solids and fouling existing treatment methods. Keeping RO membranes clean against fouling requires additional steps and “pretreatments” that add cost, salt, chemicals, wastewater, and energy. The need to operate, maintain, and supply the resulting complex trains of water purification equipment favors large scale water purification factories and associated expensive pipeline grids. RO used with groundwater without pretreatment steps suffers from low water recovery. Low water recovery depletes aquifers and increases the cost of wastewater disposal. Ultrapure water purification for green ammonia and hydrogen multiplies the costs and complexity involved.

An inexpensive water purification technology that works with minimal need to be maintained, operated, with reduced footprint, and which works reliably onsite would have multiple uses from drinking water to industry and agriculture.

A competent onsite water purification technology will help enable onsite green hydrogen and green ammonia production for use in farm equipment and farm fertilizer. An inexpensive, simple to use method that upgrades brackish water could be used to improve health and productivity of livestock, aquaculture, and agricultural plants. The ability to purify brackish water would reduce stress among competing uses for water by making supply more robust against shortages, natural or man-made.

This bold and sweeping vision is achievable with support for better water purification technology. Marc Andelman’s inventive contributions in water purification are currently the subject of an ongoing NSF seed fund phase I grant[iii]. Letters of support are required for a significant additional phase II award.

Accomplishments of Marc Andelman and his Inventions in Capacitive Deionization

Capacitive deionization represents a fundamental new method in water purification. The modern field of capacitive deionization (CDI) begins with Marc Andelman's early 1990s patents. At this time, these inventions were called "Flow Through Capacitors". Andelman's 1991 patented invention[iv] was the first publication after some earlier work died out by the early 1970s. CDI has since generated intense interest to become a rapidly growing field, with its own section at the US patent office, numerous start-up companies, pilot studies, and commercial product sales. A recently published analysis of the academic literature shows an exponentially growing number of thousands of CDI publications[v]. Publications attest that capacitive deionization has lower energy usage and than RO[vi]. CDI has high water recovery[vii]. This is important to ensure aquifers are not quickly depleted and lowers disposal costs of waste brine. The basic cell, systems, and operation inventions that underpin this entire field are originally reported in Andelman's prior art patents[viii].

CDI itself is a deceptively simple idea that required further innovation by the inventor over a period of more than thirty years. In the early 2000's Andelman invented the "charge barrier flow through capacitor"[ix] to overcome low purification efficiency. This uses ion exchange membranes and is now well known as membrane capacitive deionization or MCDI. This innovation enabled market introduction. All companies selling currently marketed, workable versions of CDI use MCDI. Marc Andelman's MCDI patents were sold in 2008 to Unilever to form Voltea.com, perhaps the most well-known company in the field. There are also numerous other, mostly small companies copying exact facsimiles of this invention. Sale of MCDI products up to flow rates of 1000 m^3/day have been reported[x]. The number of companies selling MCDI products indicates the need and desire for improved water purification technology. A partial list of important examples is included in these references[xi].However, the ion exchange membranes used in MCDI are expensive and make up most of the working flow cell cost. The need to lower CDI cost is recognized in the literature[xii].

MCDI membranes contribute electrical resistance which slows down the cell. This requires a thin flow channel spacer to compensate. This thin flow spacer restricts the flow of liquid and causes a pressure drop in the 3-6 bar range. This pressure drop traps material and organics inside the flow spacer. This will eventually cause fouling in a way that cannot be washed out with chemicals. Irreversible fouling ends the cell life. Pressure drop in the MCDI flow spacer also uses extra energy. These issues became more apparent after market introduction and are probably why MCDI remains a niche product. While this pressure drop is actually very low compared to reverse osmosis (RO), in RO, the pressure drop and fouling occurs across the membrane, not the flow spacer.

Marc's inventions continue with his most recently patented 3rd generation capacitive deionization, or 3GCDI[xiii]. This was first published as "Polarized Electrode for Flow Through Capacitive Deionization"[xiv]. 3GCDI was invented to overcome the cost and operation deficiencies in MCDI. 3GCDI has since become well known in academic publications as inverted or i-CDI.

The purpose of Andelman's 3GCDI is to finally allow cost engineering of CDI. 3GCDI works without the expensive ion exchange membranes of MCDI. The lack of resistive membranes in 3GCDI has an additional benefit of enabling use of an ordinary open, flow spacer that operates at sub bar or gravity fed pressure drop. This is much less likely to entrain materials, foul, and fail. A 3GCDI bench pilot experienced no deterioration in a one month test against hot, organic laden, industrial laundry water. MCDI failed within a few days against this feed.

The materials used in 3GCDI include activated carbon. This is one of the world's highest volume commodities, already used in water. The substances used to functionalize the activated carbon electrodes are likewise inexpensive commodities, namely surfactants, such as used in soaps, cosmetics, or food emulsifiers. Other materials are inexpensive graphite foil current collectors, inexpensive plastic flow spacer, and a cartridge holder. Electronics are being upgraded to low current, higher voltage series designs analogous to electric vehicles. This will eliminate expensive bus bars and high amperage power supplies. This promises substantial cost reduction. This work is currently the subject of an ongoing NSF seed fund grant[xv].

Marc's earlier MCDI invention has found use in commercial agriculture. Examples include an excellent, recent study in Morocco using a Voltea MCDI system to upgrade brackish water to irrigate Argan trees[xvi], a commercial system for greenhouse crops[xvii], solar powered CDI[xviii], on site use on small, remote farms[xix], etc. Livestock can suffer from high t.d.s in brackish water[xx] and represent an obvious application for an improved water purification technology that can operate in remote locations with solar power and minimal maintenance. The combination of CDI with solar power would be especially good for the livestock watering application. A number of publications combine CDI with solar power, including the recent Morocco one[xxi]. Recent publications describe use of capacitive deionization to remove nitrate in aquaculture[xxii]. Direct food applications include use in food processing, for example purification of sugar syrup by Cargill[xxiii], and reduction of salts in whey[xxiv]. Customers for drinking water compete with agricultural uses. Oxfam had a recent project to test MCDI for brackish water in the Gaza strip[xxv].

3GCDI should find use in the production of green fertilizer. Green ammonia and green Hydrogen used to make ammonia or run farm equipment are manufactured by wind or solar powered electrolyzers. This process requires ultrapure water to protect expensive parts in this equipment. For example, proton exchange membranes used in electrolyzers cannot tolerate even minute amounts of minerals in t.d.s and especially ions like calcium. Present day ultra-pure water systems have many complex steps and significant footprint, costs, and waste. This is true even when using municipal water and gets more expensive with non-traditional brackish water[xxvi]. Such a complex technology does not scale down well nor is well suited for remote locations onsite at farms. 3GCDI will greatly simplify ultrapure water production by either eliminating or reducing many steps in the process. 3GCDI has worked well in a bench pilot on hard mineral laden water. Examples of Andelman's earlier MCDI inventions have been documented for ultrapure water production[xxvii] . MCDI is commonly sold for mineral removal as a saltless water softener[xxviii]. 3GCDI will do the same at lower cost and operation risk. Independent publication documents a version of 3GCDI for mineral removal[xxix]. Both MCDI and 3GCDI are best used in low salinity brackish water. Further development and cost engineering of 3GCDI, maybe even requiring a future 4th generation CDI that could download from the universe, holds the possibility open to expand the upper practical concentration limit, possibly including to seawater.

References

[i] https://www.usgs.gov/special-topics/water-science-school/science/where-earths-water?qt-science_center_objects=0#qt-science_center_objects)
[ii] https://phys.org/news/2017-04-usgs-vast-reserves-salty-underground.html
[iii] https://seedfund.nsf.gov/awardees/history/details/?company=mespilus-inc
[iv] US5192432A Flow Through Capacitor priority date 09/15/1991, https://patentimages.storage.googleapis.com/83/41/74/982e8459d003ba/US5192432.pdf

[v] https://www.sciencedirect.com/science/article/pii/S0011916422000170
[vi] https://www.sciencedirect.com/science/article/pii/S0011916419322003

[vii] https://voltea.com/wp-content/uploads/2021/01/402D102_Rev06_Voltea-CapDI-Tech-Specs-2020-LR.pdf
[viii] A selection of Andelman's more important CDI inventions is summarized below.

US10294131B2 3GCDI, membrane-less CDI, also known as inverted or i-CDI.
US 6778378 B1 Self-sealing cell design that does not require gaskets.
US6709560B2 The original membrane capacitive deionization (MCDI). This is the first mention of the importance of charge efficiency for a useful device.
US6628505 B1 A true series flow cell with floating electrodes
US5620597 A First description of non-fouling, open flow path spacers in CDI
US5415768 A Many first described cell geometries with flow by electrodes.
US5360540 A Early CDI with first flow-through electrodes
US5192432A, and US5196115 A , Flow Through Capacitor priority dates 11/15/1991 and 9/15/1991 and The first modern CDI patent or publication. This contains the first modern design concepts universally employed since. This describes a flow cell with multiple thin, high capacitance, low resistance electrode layers, use of high surface area activated carbon, together with facing, thin low resistance current collectors.

[ix] https://patentimages.storage.googleapis.com/9a/3a/8a/6b5d42e4de0494/US6709560.pdf
[x] https://www.filtsep.com/content/features/voltea-helps-secure-water-supply-for-manufacturer-in-south-africa/

[xi] Voltea.com- formed as a Unilever start up through the acquisition of Marc Andelman's earlier MCDI and early CDI patents.

Estpure- a Chinese company, advertised through Australia 2023-09-taste-of-research-CDI-brochure (unsw.edu.au)

Evapco- a cooling tower company that developed my invention to increase cycles of concentration https://www.evapco.com/products/water-treatment-systems/water-savertm

Idropan- a small family run Italian company that sold a system to Oxfam for use in Libya, reported here

https://www.oxfamwash.org/en/innovation/_future/desalination-innovation-project.pdf

Innodi-a small Indian start up marketing water purification kiosks https://innodi.in/

Pureechem https://www.youtube.com/watch?v=F_TB_6cNwwA

[xii] https://pubs.acs.org/doi/10.1021/acsestengg.0c00094
[xiii] US 20140346046 A1

[xiv] https://patentimages.storage.googleapis.com/48/6d/00/cf6de8f3d42632/US10294131.pdf
[xv] https://seedfund.nsf.gov/awardees/history/details/?company=mespilus-inc
[xvi] https://www.mdpi.com/2077-0375/13/7/668

[xvii] https://www.youtube.com/watch?v=hWegaI3Sa6E&t=10s
[xviii] https://waterpartnership.org.au/wp-content/uploads/2018/05/kovalskyUNFAO.pdf

[xix] https://www.icid.org/wif3_bali_2019/wif3_3-1_17-min.pdf

[xx] https://www.agric.wa.gov.au/livestock-biosecurity/water-quality-livestock
[xxi] https://pubmed.ncbi.nlm.nih.gov/37505034/
[xxii] https://projects.au.dk/nordforsk/capacitive-deionization-purification-of-aquaculture-water-nordforsk-aarhus-university/capacitive-deionization-activities-nordforsk-aarhus-university, https://nmbu.brage.unit.no/nmbu-xmlui/handle/11250/3081315
[xxiii] https://patentimages.storage.googleapis.com/37/e8/a5/ac4854669e5710/US10463064.pdf
[xxiv] https://minerva-access.unimelb.edu.au/items/f3b2622f-7cc8-5b57-ac03-2ddb33df9f3d

[xxv] https://www.oxfamwash.org/en/innovation/_future/desalination-innovation-project.pdf

[xxvi] This video by a major supplier is very telling. They let on the cost as not significant, only 5 – 10 cents per kg Hydrogen. This ignores that fact that customers will leave for a penny in commodities, and, seems to only apply at large scale using municipal water. The Q&A section is important..
https://www.youtube.com/watch?v=6ppeXSEvebA

[xxvii] Ultrapure references:

https://www.sciencedirect.com/science/article/abs/pii/S0376738812002657

https://www.tandfonline.com/doi/abs/10.1080/19443994.2013.873352

[xxviii] https://voltea.com/residential/
[xxix] https://pubs.acs.org/doi/epdf/10.1021/acsomega.9b02330