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#### Review

# Various cell architectures of capacitive deionization: Recent advances and future trends



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#### ABSTRACT

Substantial consumption and widespread contamination of the available freshwater resources necessitate a continuing search for sustainable, cost-effective and energy-efficient technologies for reclaiming this valuable life-sustaining liquid. With these key advantages, capacitive deionization (CDI) has emerged as a promising technology for the facile removal of ions or other charged species from aqueous solutions via capacitive effects or Faradaic interactions, and is currently being actively explored for water treatment with particular applications in water desalination and wastewater remediation. Over the past decade, the CDI research field has progressed enormously with a constant spring-up of various cell architectures assembled with either capacitive electrodes or battery electrodes, specifically including flowby CDI, membrane CDI, flow-through CDI, inverted CDI, flow-electrode CDI, hybrid CDI, desalination battery and cation intercalation desalination. This article presents a timely and comprehensive review on the recent advances of various CDI cell architectures, particularly the flow-by CDI and membrane CDI with their key research activities subdivided into materials, application, operational mode, cell design, Faradaic reactions and theoretical models. Moreover, we discuss the challenges remaining in the understanding and perfection of various CDI cell architectures and put forward the prospects and directions for CDI future development.

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List of al	breviations	i-CDI	Inverted capacitive deionization
		IE	Ion exchange
3D	Three-dimensional	IEMs	Ion exchange membranes
AC	Activated carbon	MCDI	Membrane capacitive deionization
AEM	Anion exchange membrane	MCDC	Microbial capacitive desalination cell
CC	Constant current	MC-MCDI	multichannel membrane capacitive deionization
CDI	Capacitive deionization	mD	Modified Donnan
CEM	Cation exchange membrane	ND	Neutralization dialysis
CID	Cation intercalation desalination	NF	Nanofiltration
CV	Constant voltage	NiHCF	Nickel hexacyanoferrate
DO	Dissolved oxygen	PTFE	Polytetrafluoroethylene
ED	Electrodialysis	PVA	Poly(vinyl alcohol)
EDLs	Electric double layers	PVDF	Polyvinylidene fluoride
FCDI	Flow-electrode capacitive deionization	RCD	Reverse-current desorption
FCND	Capacitive neutralization deionization with flow	RO	Reverse osmosis
	electrodes	SAC	Salt adsorption capacity
GCS	Gouy–Chapman–Stern	SHE	Standard hydrogen electrode
GO-QC	Graphene oxide-graft-quaternized chitosan	XPS	X-ray photoelectron spectroscopy
HCDI	Hybrid capacitive deionization	ZVD	Zero-volt desorption

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#### 1. Introduction

The stress of acquiring affordable clean water is increasing around the globe in the face of climate change, population growth, industrial development, water contamination and limited availability of freshwater (Elimelech and Phillip, 2011; Porada et al., 2013b; Tang et al., 2017a; Yin et al., 2013). Owing to rich resources, desalination of sea or brackish water is conducive to increasing the fresh water supply beyond what is available from the hydrological cycle. With advantages of low energy consumption (i.e., enabling ion removal at room temperatures, low pressures and low voltages with additional possibility of energy recovery), low environmental impact (i.e., without the use of any added chemicals or the generation of hazardous substances), simple equipment structure and convenient operation, capacitive deionization (CDI) has emerged as a promising alternative to established water desalination technologies such as reverse osmosis, electrodialysis and thermal distillation, especially for desalination of waters with low to medium salinity (Suss et al., 2015; Tang et al., 2016a, 2016b; 2017b; Yin et al., 2013; Zhang et al., 2018a). The study of CDI dates back to the late 1960s when it was called "electrochemical demineralization", and the subsequent four decades saw only intermittent advances to this technology (Porada et al., 2013b). Over the last two decades, however, an exponential increase in the academic interest in CDI technology has occurred with various CDI cell architectures constantly springing up (Fig. 1), leading to tremendous advances in the CDI field.

CDI is characterized by the facile removal of charged ionic species from aqueous solutions via electrostatic or electrochemical interactions. A conventional CDI cell consists of two graphite



**Fig. 1.** (a) Evolution of the number of publications concerning CDI since the year 2000. The insert pie graph exhibits the percentage of the scientific reports of various CDI cell architectures from 2016 to the present. The data comes from "Web of Science". (b) Timeline displaying the years when various CDI cell architectures emerged and the corresponding seminal work.

current collectors facilitating electron transfer, two porous carbon electrodes for capacitive (i.e., non-Faradaic) ion sorption and a spacer channel enabling the feed water to be transported (see Fig. 2a) (Porada et al., 2013a, b; Tang et al., 2015). This CDI cell configuration is also called flow-by CDI or CDI with flow-between electrodes (Suss et al., 2015). Upon applying a voltage or current (potential difference typically no more than 1.23 V) across the two electrodes, cations and anions in the spacer channel are attracted to the cathode (i.e., negatively charged electrode) and anode (i.e., positively charged electrode), respectively, and electrostatically held in the electric double layers (EDLs) formed at the carbon/water interface (Porada et al., 2013b), generating a stream of purified water (a step called adsorption or charging). Following ion adsorption, the electrodes can be regenerated by short-circuiting the anode and cathode or reversing polarity with the trapped ions released back into the bulk solution, generating a stream of concentrated water (a step called desorption or discharging). In this way, the purified water and brine stream are produced intermittently. When the feed water flows straight through electrodes rather than between the electrodes, and parallel to the applied electric field direction, this cell is named flow-through CDI (Cohen et al., 2011; Hawks et al., 2018) (see Fig. 2c). In 2006, one important improvement over conventional CDI is the inclusion of ion exchange membranes (IEMs) in front of the electrodes, which is called membrane capacitive deionization (MCDI) (Fig. 2b) (Lee et al., 2006). Specifically, a cation exchange membrane (CEM) is placed adjacent to the cathode and an anion exchange membrane (AEM) is placed adjacent to the anode. During charging, co-ions are expelled from the micropores but unable to penetrate the IEMs and, as a

result, stay in the macropores of the electrode. Since the macropores are always electrically neutral, the macropores could serve as extra storage space for counterions, thereby improving the ion removal performance (Biesheuvel et al., 2011; Porada et al., 2013b; Zhao et al., 2012, 2013b). Incorporation of IEMs into conventional CDI is also recognized to be an effective method to increase the lifetime of electrodes via avoiding direct water scouring and alleviating particular Faradaic reactions (Tang et al., 2017a: Zhang et al., 2018a). To improve the ion removal performance for practical applications, (M)CDI cells can be assembled in multiple pairs to construct a stack. After being placed in a housing and sealed, these stacks can be connected in parallel or in series with regard to fluid flow. As one of the powerful advantages of CDI compared to other desalination technologies, in parallel with ion desorption, the energy used to charge the electrodes during desalination can be partially recovered and utilized to charge another (M)CDI cell operating in the ion adsorption step (see Fig. 3) or stored in an energy storage medium such as a supercapacitor for later use (Alkuran et al., 2008; Han et al., 2015; Kang et al., 2016; Pernía et al., 2012; Tan et al., 2018).

Flow-by CDI and MCDI are the most widely studied and utilized cell architectures in the CDI field. In recent years, there has been a fast proliferation of novel CDI cell architectures including inverted capacitive deionization (i-CDI) (Gao et al., 2015a, b), flow-electrode capacitive deionization (FCDI) (Jeon et al., 2013), hybrid capacitive deionization (HCDI) (Lee et al., 2014), desalination battery (Pasta et al., 2012), cation intercalation desalination (CID) (Smith and Dmello, 2016), and these have introduced several unique features and new functionalities to this field. Flow-by CDI, MCDI, flow-



Fig. 2. Typical cell architectures of various CDI: (a) Flow-by CDI, (b) Membrane CDI, (c) Flow-through CDI, (d) Inverted CDI, (e) Flow-electrode CDI, (f) Hybrid CDI, (g) Cation intercalation desalination, and (h) Desalination battery.



**Fig. 3.** Schematic of a CDI method with an energy recovery control system. Buck-boost topology is used for the energy transfer in order to achieve both high efficiency and good dynamic behavior. Reproduced with permission from Pernía et al. (2012). Copyright 2012 IEEE Xplore Digital Library.

through CDI, i-CDI and FCDI remove ions via the mechanism of non-Faradaic process (i.e., electrostatic and capacitive effects). The i-CDI cell arises from the modification of flow-by CDI through the use of an anode with net negative surface charge and a cathode with net positive surface charge (Fig. 2d) (Gao et al., 2015a). It exhibits excellent operation longevity and an inverted adsorptiondesorption behavior to the flow-by CDI with cell charging leading to ion desorption from the EDLs of the electrodes and cell discharging by short-circuiting the anode and cathode leading to ion adsorption (Gao et al., 2015b; Oyarzun et al., 2018). The FCDI cell arises from the modification of MCDI through the use of flowing electrodes made of carbon suspension instead of the fixed electrodes between current collectors and IEMs (Fig. 2e). FCDI enables two major benefits relative to conventional (M)CDI. One is the continuous ion removal and the steady production of desalted water, as electrode regeneration can occur as a separate process downstream of the cell (Choo et al., 2017; Rommerskirchen et al., 2018; Yang et al., 2017a). Another is the capability of desalinating high-salinity feed water due to the infinite ion adsorption capacity of the flow-electrode achieved by continuously introducing uncharged carbon particles into the charging cell (Doornbusch et al., 2016; Jeon et al., 2013; Suss et al., 2015). In terms of HCDI, desalination battery and CID, these cells remove ions via the mechanism of Faradaic process (i.e., reversible redox reactions). Generally, the HCDI cell consists of a Faradaic (i.e., battery) electrode for cation adsorption/desorption and a capacitive electrode for anion adsorption/desorption (Byles et al., 2018; Siekierka et al., 2018). An AEM could be placed adjacent to the capacitive electrode to enhance HCDI's performance (Fig. 2f). The desalination battery cell is composed of two different battery electrodes (one for cation adsorption/desorption and the other for anion adsorption/desorption) (Fig. 2h) (Shanbhag et al., 2017; Shapira et al., 2018). The CID cell is constructed by employing Faradaic cation intercalation materials for both electrodes with the electrodes separated by an AEM (Fig. 2g) (Lee et al., 2018a; Singh et al., 2018; Smith and Dmello, 2016). Owing to the superior ion sorption capacity of battery electrodes compared to traditional capacitive electrodes, HCDI, desalination battery and CID are receiving increasing attention in recent years (Suss and Presser, 2018).

The CDI research field is rapidly growing and evolving. Nevertheless, an informative study to provide a deep understanding of CDI technologies is still missing in the literature. In this work, we comprehensively reviewed the recent advances and progress made in various cell architectures of CDI, including flow-by CDI, MCDI, flow-through CDI, i-CDI, FCDI, HCDI, desalination battery and CID. Current challenges associated with the development and practical applications of various CDI, and the opportunities for improving the cell design are discussed. Future prospects on the emerging trends in various CDI cell architectures are also presented.

#### 2. Cells with capacitive electrodes

## 2.1. Flow-by capacitive deionization and membrane capacitive deionization

Flow-by capacitive deionization (Flow-by CDI) and membrane capacitive deionization (MCDI) are the two most common cell architectures in the use of CDI for water treatment. A remarkable number of innovations have been observed with key aspects focusing on materials, application, operational mode, cell design, Faradaic reactions and theoretical models.

#### 2.1.1. Materials

As a key component in both flow-by CDI and MCDI systems, the porous electrode plays a vital role in the ion removal process because its physical and chemical properties directly determine the salt adsorption capacity (SAC), charge efficiency, desalination rate and performance stability of the cell (Huang et al., 2017c; Liu et al., 2015, 2017b; Oladunni et al., 2018). Ideal candidates for electrode materials should possess the properties of excellent electrochemical stability, low cost, large ion-accessible specific surface area, fast ion mobility within the pore network, high electronic conductivity, low contact resistance between the electrode and the current collector, good wettability and process-ability, and desirable bio-inertness (Huang et al., 2017c; Liu et al., 2015; Porada et al., 2013b). Since carbon-based electrodes meet most of the abovementioned characteristics, they have been widely exploited as electrodes in the (M)CDI units. It is no exaggeration to say that the majority of effort and focus in flow-by CDI and MCDI research have been put into the synthesis and development of better electrode materials.

So far, many forms of carbon-based electrode materials have been investigated, including the classical materials like carbon aerogels (Farmer et al., 1996; Jung et al., 2007), activated carbon (Chen et al., 2011; Zou et al., 2008), activated carbon cloth (Gao et al., 2016), activated carbon fibers (El-Deen et al., 2014a; Wang et al., 2012), and the new materials like carbide-derived carbons (Porada et al., 2012, 2013a), mesoporous carbon (Li et al., 2009b, 2017b), carbon nanotubes (Dai et al., 2005; Wang et al., 2007; Yang et al., 2014), graphenes (Li et al., 2009a; Liu et al., 2017c; Wang et al., 2013), carbon-based composites (carbon-carbon composites, carbon-metal oxide composites, carbon-polymer composites and carbon-polymer-metal oxide composites) (Liu et al., 2015; Oladunni et al., 2018). Among various carbons, activated carbons stand out because they are usually the most cost-efficient materials thereby particularly attractive for widespread commercial applications, though other carbon materials such as carbon nanotubes, graphenes and carbide-derived carbon might possess more superior physicochemical properties and desalination performance. Carbon-based composite materials that take advantage of the merits of carbon and other constituent materials have become popular recently for flow-by CDI and MCDI electrodes due to the relatively low SAC of single component carbon material. The additional carbon components for the carbon-carbon composites can potentially enhance the desalination performance of pristine carbon materials primarily via adjusting the intrinsic pore size distributions, improving wettability, providing larger ionaccessible specific surface area and higher electronic conductivity (Liu et al., 2015, 2017b). The carbon-metal oxide composites might exhibit improved desalination performance compared with

pristine carbon materials mainly attributed to the increase in specific capacitance, improvement in wettability, inhibition of physical adsorption of ionic species affecting the targeted ion adsorption, or alteration of the surface zeta-potential of the carbon electrodes to enhance the charge efficiency (Liu et al., 2015, 2017b; Oladunni et al., 2018). Some examples of metal oxides incorporated into carbon materials are TiO<sub>2</sub> (Kim et al., 2014; Liu et al., 2013; Yin et al., 2013), MnO<sub>2</sub> (Li and Park, 2018; Liu et al., 2016c; El-Deen et al., 2014c), ZnO (Myint et al., 2014; Myint and Dutta, 2012), CeO<sub>2</sub> (Yin et al., 2013), SnO<sub>2</sub> (El-Deen et al., 2014b), ZrO<sub>2</sub> (Yasin et al., 2016, 2017), Fe<sub>2</sub>O<sub>3</sub> (Yin et al., 2013) and Fe<sub>3</sub>O<sub>4</sub> (Gu et al., 2015; Li et al., 2016), among which MnO<sub>2</sub> and TiO<sub>2</sub> have the advantages of low cost, being eco-friendly, and ease of anchoring into a carbon structure. Most recently, Shi et al. (2018) coated manganese oxides  $(MnO_x)$  onto the vertically aligned carbon nanotubes and found that the composites are endowed with outstanding specific capacitance and exhibited a remarkable sodium ion adsorption capacity (2-fold higher than that of pristine vertically aligned carbon nanotubes). As for the carbon-metal oxide composites, it is also important to point out that, stability of the metal oxide under the applied potential and solution environment is also critical to the electrode performance. For instance, ZnO is unstable in both acidic and basic solutions (Liu et al., 2015). The dissolution of such metal oxides will result in contamination of the purified water and a decrease in electrode's lifetime. Furthermore, water electrolysis and other parasitic redox reactions (e.g., reduction of dissolved oxygen, oxidation of carbon and chloride ions) may occur more easily when using the carbon-metal oxide composite materials because the metal oxide may change the point of zero charge of the electrode to be close to the potential of the redox reactions (Liu et al., 2015). The incorporation of polymers into carbon materials may contribute to the ion removal performance with their suitable physicochemical properties such as pseudo-capacitance, inclusion of oxygen- and nitrogen-containing functional groups, or ionexchange ability (Liu et al., 2015, 2017b). Among polymers utilized in the carbon-polymer composites, polyaniline, polypyrrole, chitosan and ion-exchange polymers are of particular interest (Li et al., 2017a; Ma et al., 2016a; Wang et al., 2014; Yan et al., 2014).

Present research also focus on tuning the surface chemistry of the existing types of carbon-based electrode materials (Gao et al., 2016; Wu et al., 2015a). The surface properties of electrode materials, such as wettability, hydrophilicity and surface charge, have a great impact on the desalination performance. Surface-tuned carbon-based electrode materials doped with heteroatoms or grafted with functional groups enable good wettability and electrical conductivity as well as a high specific capacitance, which is beneficial to improving the desalination performance (Zhang et al., 2018d). However, a decrease in the adsorption sites might result from the blockage of pores by large molecules. Advantages always seem to be accompanied by trade-offs in these kinds of surfacetuned electrode materials. As such, there exists substantial room for stimulating research and development of high-performance carbon-based materials for flow-by CDI and MCDI electrodes.

For making CDI electrodes, we cannot use single carbon particles but need a film composed of such particles. Film electrodes for flow-by CDI and MCDI cells are commonly fabricated by compressing the slurry mixture of carbon materials (active material), a conductive additive (e.g., carbon black) and a polymeric binder (~10 mass%) into a sheet followed by a drying process (Porada et al., 2013b). Particularly, the binder plays a key role in determining the mechanical strength, electrical conductivity and performance of carbon electrodes. Hydrophobic polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) are often used as the electrode binder. However, these binders can reduce the wettability of an electrode and some portion of the electrode surface area may not be wetted, which may result in a decrease in ion adsorption capacity. Additionally, the rigidness of and PTFE and PVDF can generate the mechanical crack at the electrode interface and then lead to loss in electrode performance (Asquith et al., 2015; Jain et al., 2018). Hydrophilic polymer binders such as poly(vinyl alcohol) (PVA) (Jain et al., 2018; Park and Choi, 2010), poly(vinyl acetate) (PVAc) (Park et al., 2011a), and poly(arylene ether sulfone) copolymers (Asquith et al., 2015) have been reported to be good candidates for increasing the wettability of polymer-bonded carbon electrodes, but their swelling and degradation tendency in aqueous solution are undesirable, though a great degree of crosslinking with glutaric acid is effective to solve this problem (Park and Choi, 2010). In the efforts to find a better electrode binder, an organic-inorganic hybrid binder (i.e., introduction of silicate into a resin binder) has been also explored in a recent study to fabricate robust activated carbon electrodes (Xie et al., 2017).

In addition to the electrode materials, there are innovations in membranes for MCDI cells (Ahualli et al., 2017; Lee et al., 2011; Pan et al., 2018; Tian et al., 2014). It is well known that ion adsorption capacity and charge efficiency can be increased significantly by applying a MCDI process, a process combining flow-by CDI with IEMs. However, the cost of the commonly utilized commercial IEMs remains prohibitively high for large-scale applications. In addition, the IEMs are usually thick (unfavorable to assembling) and have high electrical resistance. Moreover, the weak contact adhesion between the electrodes and the IEMs might produce a noticeable contact resistance. To overcome these limitations, various ionexchange polymers have been proposed to replace the IEMs in MCDI devices. Numerous studies have indicated that the cell assembled with carbon electrodes coated with a thin layer of ionexchange polymers exhibits a better desalination performance than the conventional flow-by CDI cell and, in some cases, an improved desalination performance than the conventional MCDI cell. For example, Liu et al. (2014) fabricated a modified MCDI cell by introducing the anion exchange polymer (dimethyl diallyl ammonium chloride) and cation exchange polymer (polyethyleneimine) onto the carbon nanotube electrodes and found that the modified MCDI cell exhibited a high NaCl removal of 93%, much higher than that of conventional flow-by CDI cell (25%) or the MCDI cell with commercial IEMs (74%). The reported cationexchange polymers so far include polyethyleneimine (Liu et al., 2014), cross-linked poly(vinyl alcohol) with sulfosuccinic acid (Kim et al., 2016a), and poly(styrene sulfonic acid-co-maleic acid) (Kim et al., 2016a), sulfonated bromomethylated poly(2,6dimethyl-1,4-phenylene oxide) (Lee et al., 2011), poly(sodium 4styrenesulfonate) (Ahualli et al., 2017) while anion-exchange polymers include dimethyl diallyl ammonium chloride (Ahualli et al., 2017; Liu et al., 2014), aminated polysulfone (Kim et al., 2016a), cross-linked guaternized poly(vinyl alcohol) with glutaraldehyde (Jain et al., 2018; Tian et al., 2014), aminated bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (Lee et al., 2011). Alternatively, it is possible to directly graft the carbon electrodes with ion-selective functional groups which can act as coatings similar to the IEMs without adding much electrical resistance (Qian et al., 2015; Yang et al., 2013).

Generally, there are two primary aims in optimizing the electrode and membrane materials: enhancing desalination performance and maintaining performance stability. Guided by the two goals, we expect that considerable efforts will continue to be dedicated to the development of new electrode and membrane materials that could provide a desirable desalination performance or performance stability, among which construction of cells consisting of asymmetric porous carbon-based electrodes will represent an important research direction (Choi et al., 2018; Wu et al., 2015a). A third goal attracting increasing interest is the selective removal of specific ions. As such, selection or fabrication of electrodes and membranes that permit selective removal of cations and/or anions is also a critical issue in upcoming related research.

#### 2.1.2. Application

Flow-by CDI and MCDI are currently being actively explored for water treatment with particular applications in brackish water desalination and wastewater remediation. Compared to the dominating desalination technologies by far, such as reverse osmosis and multi-stage flash distillation, flow-by CDI and MCDI require less energy for desalination of water with a low or moderate salt content (roughly below  $2 \text{ g L}^{-1}$ ) (Porada et al., 2013b; Suss et al., 2015; Zhang et al., 2018a). Part of the reason is that, rather than extracting the majority compound (water molecules) from the salt solution as in reverse osmosis and multi-stage flash distillation, flow-by CDI and MCDI remove the minority compound (NaCl) from the feed water (Porada et al., 2013b; Suss et al., 2015). Starting from the 1990s when the interest in CDI revived, extensive studies have been carried out to improve the performance of flow-by CDI and MCDI in brackish water desalination with research efforts ranging from fabrication of new electrode/membrane materials (Ahualli et al., 2017; Huang et al., 2017c), development of new operational modes (Garcia-Quismondo et al., 2016; Zhang et al., 2017), design of novel cell configurations (Bian et al., 2015; Kim et al., 2018b), mitigation or elimination of the undesired Faradaic reactions (Choi, 2014; Zhang et al., 2018a) to use of theoretical methods for parameter optimization (Hawks et al., 2018; Tang et al., 2015). Flow-by CDI and MCDI are not suitable for seawater desalination due to the limited salt adsorption capacity and the higher energy consumption than that of reverse osmosis for treating seawater (Porada et al., 2013b). In wastewater remediation application, flowby CDI and MCDI have proven the ability to remove various types of ionic pollutants including heavy metals (e.g., Cu(II) (Huang et al., 2014; Liu et al., 2017a), Cr(III) (Huang et al., 2016), Cr(VI) (Hou et al., 2018; Liu et al., 2011), Pb(II) (Liu et al., 2017c; Yang et al., 2014), Cd(II) (Chen et al., 2017d; Huang et al., 2016), V(V) (Bao et al., 2018), Fe(II) (Chen et al., 2017d; Liu et al., 2017a), Fe(III) (Chen et al., 2017d; Li et al., 2010), As(III) (Fan et al., 2016, 2017), As(V) (Fan et al., 2016, 2017)), inorganic contaminants (e.g., Ca<sup>2+</sup> (Chen et al., 2017d; Seo et al., 2010), Mg<sup>2+</sup> (Chen et al., 2017d), NO<sub>3</sub> (Tang et al., 2015; Yeo and Choi, 2013), F<sup>-</sup> (Tang et al., 2015, 2016b), Br<sup>-</sup> (Liu et al., 2016a), SO<sub>4</sub><sup>2-</sup> (Tang et al., 2017b; Thamilselvan et al., 2018), B(OH)<sub>4</sub> (Avraham et al., 2011), NH<sub>4</sub> (Wimalasiri et al., 2015), phosphate (Huang et al., 2017a)) and organic contaminants (e.g., ionizable dyes (Chen et al., 2017c; Shi et al., 2014; Shi and Zhitomirsky, 2015a, b) and antibiotics (Wang et al., 2018)). Here, it should be pointed out that some of the ionic pollutants such as arsenic, chromium, phosphate are amphoteric ions which are a strong function of electrolyte pH values. As the electrolyte pH values can fluctuate while charging (M)CDI cells, the removal process of such ions becomes complicated. Meanwhile, it is worth noting that some metal ions, for example copper, might be reduced to elemental copper and deposited on the electrodes during charging step (Huang et al., 2014). This ion removal process is based on the mechanism of metal electroplating instead of capacitive deionization and is unfavorable to the performance stability of (M) CDI as electrode regeneration is difficult. For both brackish water desalination and wastewater remediation, concentrated streams would be more or less produced during desorption. How to dispose the concentrated streams appropriately is a problem confronting flow-by CDI and MCDI's applications. While directly discharging the brine solution from brackish water desalination into the environment appears to be viable, dealing with the concentrated solution from wastewater remediation normally requires more complex post-treatment procedures, among which recovery of specific ions from the concentrate solution, e.g., recovery of sulfate via precipitation of high value minerals (Tang et al., 2017b), recovery of ammonium via air or steam stripping (Zhang et al., 2018b) and recovery of palladium via electrowinning (Kim et al., 2017b), represents an important research direction, but the premise is that the concentration of the target ion should be high enough.

Aside from the applications of brackish water desalination and wastewater remediation, flow-by CDI and MCDI have also been investigated as a tool towards disinfection (El-Deen et al., 2016; Ge et al., 2018; Laxman et al., 2015; Pandit et al., 2017; Wang et al., 2015a). For example, a high-performance capacitive deionization disinfection cell was demonstrated by Wang et al. (2015a) where the activated carbon (AC) electrodes were coated with a thin layer of cationic nanohybrids of graphene oxide-graft-quaternized chitosan (GO-QC) with inherent antimicrobial activity. The GO-QC/AC electrode could achieve ultrahigh killing (i.e., 99.9999%, 6 log reduction) of  $10^6$  CFU mL<sup>-1</sup> E. coli in water flowing continuously through the cell. There is a recent report on the application of flowby CDI for water disinfection using commercially activated carbon cloth electrodes but most of the bacteria were not killed but only electro-adsorbed on the electrodes as bacterial cells carry negative charges induced by the presence of phosphates and lipopolysaccharides (Laxman et al., 2015). More recently, Pandit et al. (2017) found that, for both positive and negative applied potentials with a voltage window of 0.9 V, there was an inverse relationship between the formation of Pseudomonas aeruginosa biofilm on the carbon electrodes and the magnitude of the applied potential. It was believed that the relatively high potentials affected the redox potential across the cell membrane and disrupted redox homeostasis, thereby inhibiting bacterial growth. With a high applied voltage (>1.5 V), antimicrobial activity may also result from byproducts generated in situ (e.g., chlorine, oxidizing radicals, hydrogen peroxide) through the occurrence of Faradaic reactions in a (M)CDI cell (Ge et al., 2018).

Moreover, flow-by CDI and MCDI have been explored for selective removal of a specific ion from multi-ionic solutions. Assuming that the initial concentrations of ion *i* and ion *j* are equal in the treated water, flow-by CDI and MCDI might present weak adsorption selectivity between the two ions because of their different diffusion coefficient, ion charge number hydrated radius and electronegativity, and the differential separation may become more evident with operating parameters appropriately adjusted (Dykstra et al., 2016; Tang et al., 2017b). To increase the extent of preferential ion adsorption, certain improvements could be made, for instance, coating the carbon electrode surface with a material with high selectivity towards one specific ion (Su et al., 2017; Zuo et al., 2018), or synthesizing a composite electrode by mixing carbon particles with a material with high affinity towards the ion of concern (Lee et al., 2017a; Su and Hatton, 2017). An alternative approach to achieve preferential removal of a certain ion is utilizing an asymmetric CDI cell to selectively enable electro-oxidation or electro-reduction of one ion species while removing the other ion species via Coulomb force. This has been recently well demonstrated in the case of the selective removal and recovery of Br<sup>-</sup> from a mixed solution of Br<sup>-</sup> and Cl<sup>-</sup> using an asymmetric CDI cell where the applied potential is divided between the positive and negative electrodes asymmetrically (Cohen et al., 2018). Upon electrooxidation of Br<sup>-</sup>, Br<sub>2</sub> molecules are formed and physically adsorbed on the surface of the positive electrodes. When discharging the electrodes, Br<sub>2</sub> molecules are reduced back to Br<sup>-</sup> and return to the solution. As a key component in MCDI cells, membrane might also play an important role in the selective ion removal if designed appropriately. One specific example is that, in a MCDI cell where the CEM was replaced by a monovalent cation permselective exchange membrane, a selective removal of monovalent and divalent

cations was achieved, thereby producing divalent cation-rich solution. The cation removal selectivity could get higher when total dissolved solids concentration decreased and pH increased (Choi et al., 2016).

In addition to the above applications solely based on CDI technologies, flow-by CDI and MCDI systems can be combined with other technologies synergistically to achieve various ultimate goals (Feng et al., 2017: Forrestal et al., 2015: Hou et al., 2018: Kim et al., 2012a; Lee et al., 2009; Liang et al., 2015; Ma et al., 2015; Saleem et al., 2018; Tan et al., 2018; Wen et al., 2014). For example, by integrating a CDI system with a bioelectrochemical system, a microbial capacitive desalination cell (MCDC) could be developed to remove organics and salts simultaneously without using any external energy (see Fig. 4) (Stoll et al., 2015). Microbial degradation of organic compounds in the anode chamber generated an electron flow to reduce the electron acceptors in the cathode chamber. Taking advantage of the potential difference across the microbial anode and the air-cathode, ions in the desalination chamber were electrically adsorbed in the EDLs of porous carbon electrodes. Furthermore, the MCDC allowed for the free transfer of protons from the anode chamber throughout the reactor and thus prevented significant pH changes. A second example is combination of constant-current operated flow-by CDI system with reverse osmosis (RO) for the production of high-quality ultrapure water and freshwater from seawater (Minhas et al., 2014). A third example is combination of MCDI system with ion exchange (IE) process for nitrogen recovery from low-strength wastewater (Wang et al., 2017). MCDI acted as a pretreatment to preferentially remove the coexisting  $Ca^{2+}$  and  $Mg^{2+}$ , thereby eliminating the negative effects of  $Ca^{2+}$  and  $Mg^{2+}$  on the subsequent IE ammonium recovery process.



**Fig. 4.** Schematic diagram of a microbial capacitive desalination cell (MCDC) treatment process designed to remove organics and salts simultaneously without using any external energy. Reproduced with permission from Stoll et al. (2015). Copyright 2015 Elsevier.

With an eye towards the future, we believe that more application potentials of flow-by CDI and MCDI will be discovered. This is evidenced by the very recent work of Legrand et al. (2018) who used MCDI cells to capture  $CO_2$  in the form of bicarbonate and carbonate ions produced from the reaction of  $CO_2$  with water. Moreover, towards the applications of water desalination and wastewater remediation, research involving studying the shortterm or long-term influence of co-occurrence of inorganic compounds and natural organic matter in real waters on the performance of flow-by CDI and MCDI as well as the effective postoperational cleaning methods will be a significant part of future efforts.

#### 2.1.3. Operational mode

Generally, there are two kinds of designs for the flow-by CDI and MCDI studies with regard to fluid flow, batch mode and single-pass mode. Batch mode refers to a configuration whereby water is fed from a small container and the effluent of the CDI cells is returned to the feeding reservoir where water conductivity is measured. The recycling reservoir should be small enough so that the change in the conductivity is distinguishable and can be measured accurately. During adsorption, the measured conductivity steadily decreases until it levels off at a low value indicating saturation of the electrodes (Porada et al., 2013b; Salamat and Hidrovo, 2018). In contrast, single-pass mode refers to a configuration whereby water is fed from a large storage container and the effluent water leaving the CDI cells is either discarded or recycled to the feeding reservoir. The conductivity of the treated water is measured directly at the exit of the CDI unit. The volume of feeding reservoir should be large enough to ensure that the influent conductivity only changes slightly during successive cycles when both dilute and concentrated streams return to the feeding reservoir. During adsorption, the measured effluent conductivity will decrease rapidly and reach a minimum value upon applying a fixed charging voltage, followed by a gradual increase to the inlet value (Porada et al., 2013b). Although batch mode is simpler than single-pass mode, single-pass operation is more common and efficient for practical situations because the treated water only passes through the CDI device once instead of being recycled many times. To calculate ion removal efficiency and equilibrium adsorption capacity by flow-by CDI and MCDI cells, one needs to measure the effluent ion concentration with time. For single electrolyte, the ion concentration could be determined from the conductivity of the solution. For mixtures of electrolytes, water samples need to be collected at appropriate intervals and the ion concentrations then analyzed using analytical methods such as ion chromatography.

In addition, there are commonly two kinds of charging modes for the adsorption step (constant voltage and constant current) and three kinds of discharging modes for the desorption step (zero-volt, reverse-voltage and reverse-current) (Porada et al., 2013b) Among them, constant-voltage adsorption combined with zero-volt desorption (CV-ZVD) is the most common and classical option while constant-current adsorption combined with zero-volt desorption (CC-ZVD) or reverse-current desorption (CC-RCD) is also a good alternative for flow-by CDI and MCDI cells. Applying different operational modes for adsorption-desorption cycle may result in different desalination performance. One important choice that must be made is whether operation should be at constant voltage (CV) or constant current (CC). There are various criteria for determining this choice, such as the desire for a constant effluent ion concentration or a low energy consumption. From the perspective of effluent ion concentration, CC mode is more favorable than CV mode because, in contrast to the marked change in the outflow concentration at CV mode, a stable and adjustable effluent ion concentration can be obtained at CC mode. From the perspective of energy consumption, in literature it is often reported that CC mode is both experimentally and theoretically superior to CV mode (Han et al., 2015; Kang et al., 2014; Qu et al., 2016; Zhao et al., 2012, 2013b). Main argument in support of this claim is that in CC operation the endpoint voltage is reached only at the end of the charging step, hence accompanying with an overall lower cell voltage. However, recently, three different voices arose. Based on both experimental assessment and theoretical analysis. Wang and Lin (2018) suggested that whether CC or CV charging is more efficient for a given MCDI system is largely dependent on the target adsorption to be achieved and, to a less extent, on the kinetic rate of charging. Dykstra et al. (2018) found that, without energy recovery, there is no difference in energy consumption between CC and CV operation. If 50% of the energy released during discharge could be recovered, CC has a somewhat lower energy consumption than CV. By Fourier transforming both CC and CV signals, Ramachandran et al. (2018) found that, CC is more energy-efficient while charge efficiency is high, but at high salt concentrations CV will be more energy-efficient. In regard of the desorption step, it is worth mentioning that the reverse-voltage approach is not feasible in flow-by CDI because the ions released from one electrode can get quickly re-adsorbed into the other electrode before they exit the cells, whereas it is possible to operate at reversed voltage in MCDI as the ions released from one electrode cannot move into the other electrode because of the IEMs (Biesheuvel et al., 2011; Salamat and Hidrovo, 2018; Zhao et al., 2012).

To date, effort, although not much, has been directed towards developing new operational modes with regard to both fluid flow and power aspects of the charging and discharging modes to improve the performance (e.g., average concentration reduction, water recovery and energy consumption) of (M)CDI technologies, and some advances have been made (Gao et al., 2017; Garcia-Quismondo et al., 2013; Kim et al., 2015; Lu et al., 2017; Ramachandran et al., 2018; Saleem et al., 2016; Zhang et al., 2017, 2018c). With respect to fluid flow, Garcia-Quismondo et al. (2016) and Hassanvand et al. (2017) examined the use of a new operational procedure that utilizes a brine stream, which is more concentrated than the feed solution, to regenerate the (M)CDI unit during desorption and found that this significantly increased the energy efficiency and/or water recovery. With respect to power aspects, Gao et al. (2017) and Zhang et al. (2018c) demonstrated that using alternating polarization, i.e., reversing electrode polarity every charging step, could effectively enhance the cycling stability of flow-by CDI systems. Kim et al. (2015) described a new discharging modes for the desorption step, that is, applying a discharging voltage lower than the charging voltage but with the same

polarity, whereby the charge efficiency of a flow-by CDI cycle could be increased to values close to unity and the energy consumption could be reduced, with only a small loss of salt adsorption capacity. Further, Ramachandran et al. (2018) developed a sinusoidal voltage/current operation for flow-by CDI as an efficient method and identified a system-inherent resonant frequency that enables maximum concentration reduction, as shown in Fig. 5.

#### 2.1.4. Cell design

Besides synthesis of new electrode (or membrane) materials with improved physico-chemical properties and development of new effective operational modes, coming up with novel and superior cell designs based on fundamental structures of flow-by CDI and MCDI is also conducive to enhancing the desalination performance.

As mentioned previously, in MCDI, the incorporation of IEMs leads to a remarkable improvement in the flow-by CDI cell's desalination rate, salt removal efficiency and charge efficiency. A further enhancement of the desalination performance has been confirmed to be attainable via constructing new designs of MCDI cell. Considering that the resistance of MCDI is mainly located in the spacer compartment, Liang et al. (2013) revealed that, by packing the MCDI cell's flow chamber with ion-exchange resin granules, the modified MCDI delivered higher desalination rates, salt removal efficiency and charge efficiency than the regular MCDI. Electrochemical impedance spectroscopy analysis showed that the packing of ion-exchange resin granules greatly reduced the ohmic resistance of MCDI and, as a result, facilitated the ion transport across the flow channel and accordingly enhanced the desalination rate. In the subsequent work conducted by the same research group (Bian et al., 2015, 2016), it was found that the commercially available and inexpensive granular activated carbon particles and the activated carbon fibers exhibited similar enhancements effects when employed as the MCDI's separator packing material. Following this line of thinking, more promising alternative to the ion-exchange resin granules are expected to turn up in future research, Recently, Kim et al. (2017a) presented a novel multichannel MCDI (MC-MCDI) system by introducing two side channels surrounding the carbon electrodes while a conventional MCDI channel (i.e., middle channel) is located between an AEM and a CEM, as schematically shown in Fig. 6. At a high salinity gradient between side (1000 mM) and middle (5 mM) channels, this MC-MCDI cell configuration exhibited an excellent salt adsorption capacity (SAC) of 56 mg  $g^{-1}$  in the middle channel which was nearly four times larger than the maximum SAC achievable in a conventional CDI cell, though desalination occurred in the opposite



**Fig. 5.** Schematic of (a) a sinusoidal forcing voltage (current) applied to the flow-by CDI system as the input, (b) a sinusoidal time variation of effluent concentration as the output, and (c) a system-inherent resonant frequency that enables maximum concentration reduction for the desalinated water. Adapted with permission from Ramachandran et al. (2018). Copyright 2018 Elsevier.



Fig. 6. Multichannel membrane CDI (MC-MCDI) cell using channels and membranes: scheme (A), top view (B), components (C), and exploded view of the cell (D). Reproduced with permission from Kim et al. (2017a). Copyright 2017 Wiley Online Library.

direction of the concentration gradient. Meanwhile, the SAC was accomplished with a high charge efficiency close to unity and a low energy consumption. The performance enhancement stemmed from the enhanced capacitance at high molar strength in the side channels and the double ion-removal process during cell voltage inversion. Following this work, Kim et al. (2018a) explored and proved the feasibility of the MC-MCDI cell in semi-continuous production of clean water with the separated middle and side channels resulting in alternating desalination and regeneration. Most recently, Kim et al. (2018b) further modified the MC-MCDI cell with one side-channel filled with a highly concentrated aqueous electrolyte (1 M NaCl in H<sub>2</sub>O) and the other with a highly concentrated organic electrolyte (1 M NaClO<sub>4</sub> in propylene carbonate). The novel MC-MCDI cell using an aqueous/organic bi-electrolyte allowed extension of the cell voltage to 2.4 V and thus provided a superior SAC of  $63.5 \pm 4 \text{ mg g}^{-1}$  in the middle channel with charge efficiency of 95%. Future work may capitalize on the use of alternative electrolytes (e.g., acetonitrile) or alternative electrode material (e.g., intercalation-type material).

#### 2.1.5. Faradaic reactions

Whilst non-Faradaic processes such as capacitive ion storage and ion transport are at the heart of the CDI phenomenon, it is recognized that Faradaic reactions (i.e., redox reactions occurring on the surface of and within the carbon electrodes) also play important roles in the flow-by CDI and MCDI systems. On the one hand, as one of the two main sources of energy losses (resistive and parasitic losses) in (M)CDI (Fig. 7) (Hemmatifar et al., 2016), Faradaic reactions result in a decrease in energy efficiency since parasitic current generated by reduction or oxidation processes at the electrodes is not effective in adsorbing ions. These redox reactions may also contribute to pH fluctuations in the effluent and deterioration of electrode stability and performance (Bouhadana et al., 2011; Choi, 2014; Cohen et al., 2013, 2015; Shapira et al., 2016;



**Fig. 7.** (a) Schematic of circular flow-by CDI cells with two electrode pairs. (b) Schematic of energy pathway in a typical flow-by CDI system. A fraction of input energy Ein during charging is dissipated via resistive (EinR) and parasitic (EinP) processes and the rest is stored in the cells (Ecap). A portion of stored energy is then dissipated during discharging (EoutR and EoutP) and remaining energy is recovered (Eout). (c) Input energy, regenerated energy and lost energy of the cells. Diagonal hatched areas show series resistive energy loss and vertical hatched areas show parasitic (i.e., Faradaic) energy losses. Reproduced with permission from Hemmatifar et al. (2016). Copyright 2016 Elsevier.

Tang et al., 2017a; Yu et al., 2018). On the other hand, the in-situ formed reactive species such as hydrogen peroxide  $(H_2O_2)$  and/or free chlorine might be positively used, in combination with ultraviolet irradiation or ozone, for water disinfection and/or degradation of organic contaminants (He et al., 2016; Kim et al., 2016c; Tang et al., 2017a; Zhang et al., 2018a). There are two major types of Faradaic reactions existing in the flow-by CDI and MCDI systems, namely (i) anodic reactions associated with oxidation of the carbon electrode, chloride ions, water, etc. (ii) cathodic reactions involving dissolved oxygen (DO) reduction and other particular ions.

Carbon oxidation refers to the phenomenon that the carbon anode sacrificially takes part in oxidation processes with the carbon converted into functional groups containing C=O and carbon dioxide (Zhang et al., 2018a). Of all the anodic Faradaic reactions, carbon oxidation is the most important and attracts the most attention considering the high likeliness of its occurrence when the flow-by CDI or MCDI cell is operated routinely (the redox potential for carbon oxidation is +0.207 V/SHE) (Oh et al., 2008) and the induced negative effects that may accrue such as pore structure impairment and mass loss with subsequent decrease in carbon electrode longevity and deterioration of CDI performance (Zhang et al., 2018a). Long-term flow-by CDI experiments have been conducted by Cohen et al. (2013) (18 days) and Omosebi et al. (2014) (50 h), both of which showed reduction of the salt adsorption capacity caused by parasitic Faradaic reactions. Strategies to evaluate the anodic oxidation of carbon electrodes include X-ray photoelectron spectroscopy (XPS), scanning electron microscopy with energy dispersive X-ray mapping, Fourier transform infrared spectroscopy, acid-base titration and cyclic voltammetry (Cohen et al., 2013; Zhang et al., 2018a), among which XPS method is quite effective in detecting the variation in oxygen functional groups (reflected by O 1s spectrum) and the loss of carbon (reflected by C 1s spectrum) from the electrodes after continuous charging/discharging cycles. To mitigate and/or eliminate the anodic carbon oxidation, a few approaches can be utilized including synthesis of oxidation-resistant materials (e.g., titania-decorated carbon electrodes) (Srimuk et al., 2016, 2017c), employing novel cell architectures (e.g., inverted capacitive deionization) (Gao et al., 2015a, b), and applying appropriate operational modes (e.g., constant-current charging and periodic polarity reversal) (Dykstra et al., 2018; Gao et al., 2017; Zhang et al., 2018c). In addition to the anodic carbon oxidation, anodic oxidation of chloride ions (Cl<sup>-</sup>) and water might occur during brackish water treatment on condition that the anode potentials of flow-by CDI and MCDI cells are sufficiently positive to drive these redox reactions. Free chlorine (Cl<sub>2</sub>) could be generated through the direct oxidation of Cl<sup>-</sup> at the anode (standard electrode potential  $E^0 = +1.36$  V/SHE), followed by a hydrolysis reaction to form hypochlorous acid (HClO). HClO and its deprotonated form CIO<sup>-</sup> might be further oxidized to chlorate  $(ClO_3^-)$  at the anode (Zhang et al., 2018a). Under a higher standard electrode potential of 1.45 V/SHE, the direct oxidation of Cl<sup>-</sup> to ClO<sub>3</sub> may occur (Zhang et al., 2018a). In any cases, Cl<sup>-</sup> at the surface of the anode rather than free Cl<sup>-</sup> in solution is supposed to be the main contributor to the generation of  $ClO_3^-$ , and this has been confirmed by the studies of Lado et al. (2013) and Wouters et al. (2013) who showed that the production rate of  $ClO_3^-$  in the flowby CDI system increased with greater abundance of Cl<sup>-</sup> in the vicinity of the anode during adsorption. In terms of anodic oxidation of water, it occurs at a standard electrode potential of 1.23 V/SHE and this is the reason why the (M)CDI process is generally operated at charging voltages below 1.23 V. However, in fact, the potential difference across the cell might exceed the 1.23 V threshold to compensate for the circuit system resistance and hence no water electrolysis happens in these cases (Tang et al., 2015, 2016a; 2017b). Lastly, as a beneficial effect, anodic oxidation reactions may contribute to the removal of certain organic compounds (e.g., phenol and humic substances) (Duan et al., 2015; Liu et al., 2016a) and inorganic pollutants (e.g., arsenic(III) and bromide ion) (Cohen et al., 2018; Fan et al., 2016, 2017; Lee et al., 2016) from water through a combination of Faradaic and non-Faradaic processes.

Among the reduction reactions that take place at the cathode. dissolved oxygen (DO) reduction is the most common as DO is prevalent in feed waters to CDI cells. Our recent batch-mode CDI studies have revealed that significant concentrations of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) could be produced during charging in flow-by CDI cells with the generation of H<sub>2</sub>O<sub>2</sub> initiated by cathodic reduction of DO with subsequent consumption occurring as a result of anodic oxidation and cathodic reduction of H<sub>2</sub>O<sub>2</sub>, and the reaction rate constants increase with an increase in charging voltage (0.5-1.5 V)(He et al., 2016; Tang et al., 2017a). Kim et al. (2016c) and Yu et al. (2018) also reported the cathodic generation of  $H_2O_2$  during a single-pass flow-by CDI operation. An almost constant H<sub>2</sub>O<sub>2</sub> concentration in the effluent was observed throughout the entire charging step and the H<sub>2</sub>O<sub>2</sub> generation could provide one of explanations to the pH fluctuations. Fig. 8a schematically displayed all the Faradaic reactions that may occur in the flow-by CDI cell during charging including both cathodic reduction of DO and anodic oxidation of carbon electrode and water in the absence of the occurrence of electrolyte-mediated redox processes. In contrast to the significant amount of H<sub>2</sub>O<sub>2</sub> in flow-by CDI cells, almost no H<sub>2</sub>O<sub>2</sub> was generated in MCDI cells with H<sub>2</sub>O<sub>2</sub> concentrations relatively time invariant and typically <2 µM during charging and discharging, as indicated in Fig. 8b (Tang et al., 2017a). Owing to the attachment of IEMs to the surfaces of the carbon electrodes. accessibility of oxygen to the electrodes is limited in the MCDI case with the resultant inhibition of the occurrence of DO reduction reaction responsible for significant reduction in quantity of H<sub>2</sub>O<sub>2</sub> produced in this system. Incorporation of the membranes to act as a barrier to limit DO access to the electrode was also reported by Omosebi et al. (2014) who found more distinct perturbation of DO in flow-by CDI than MCDI during cell operation. The findings arising from these studies raise the need to re-examine the potential applications of flow-by CDI and MCDI cells. For example, despite the poorer salt removal capacity and lower charge efficiency, flow-by CDI might be a better choice than MCDI when treating source waters containing microorganisms and/or trace organic contaminants if the in-situ formed H<sub>2</sub>O<sub>2</sub> could be effectively used as a disinfectant and/or used to produce more powerful oxidants such as hydroxyl radicals. Apart from DO reduction, cathodic reduction reactions may also play an important role in the sequestration of heavy metals (e.g., Cd(II), V(V)) from water as a result of the possible deposition of the metals at the electrode (Bao et al., 2018; Huang et al., 2014, 2016; Liu et al., 2011; Yang et al., 2014).

Faradaic reactions in flow-by CDI and MCDI systems are attracting increasing attention from the academic and industrial world. Despite the achievements presented, many questions remain with additional studies required to further improve the mechanistic understanding of Faradaic reactions with the goal of effectively mitigating the negative effects of these processes whilst taking advantage of their positive effects.

#### 2.1.6. Theoretical model

While (M)CDI clearly has many attractions, it is a sophisticated technology requiring careful selection of design and operating parameters for particular source waters. Laboratory or field-based investigation of the effect of each parameter on (M)CDI performance is difficult in view of the difficulty in manipulating some parameters and the interconnectivity of others. As such, quantitative evaluation of the effect of particular parameters or design options is best achieved by developing theoretical models of key



Fig. 8. (a) Schematic diagram of all the Faradaic reactions that may occur in the flow-by CDI and MCDI cells during charging in the absence of the occurrence of electrolyte-mediated redox processes. (b) Dynamic variation of H2O2 concentration during charging and discharging in the flow-by CDI and MCDI cells at different charging voltages. Symbols: experimental data; Lines: modelling results. Adapted with permission from Tang et al. (2017a). Copyright 2017 Elsevier.

non-Faradaic and, potentially, Faradaic processes (Tang et al., 2016b). Apart from enabling optimization of both design and operating parameters, the theoretical model also serves as a useful and essential tool to reveal the underlying causes of phenomena, help to gain thorough understanding of the ion removal process and predict (M)CDI performance in all its facets including effluent ion concentration, water recovery, energy consumption, average salt adsorption rate, ion adsorption capacity, pH fluctuations, and so on (Biesheuvel et al., 2015; Hemmatifar et al., 2017; Kim et al., 2015; Porada et al., 2013a; Tang et al., 2015, 2016a, 2016b).

To describe ion storage in EDLs, an appropriate EDL structure model has to be established first. Basically, the EDL-model describes that, across the carbon/electrolyte interface in the pores inside the carbon particles, the surface electrical charge in the carbon matrix is directly charge-compensated by counterions in the electrolyte (Porada et al., 2013b). Initial well-known EDL structure models include the Helmholtz model and the Gouy--Chapman-Stern (GCS) model. However, neither of the two models properly captures the EDLs' structure along typical CDI electrodes' pore walls. The Helmholtz model assumes that counterions are all condensed in a plane right next to the carbon surface and necessitates a charge efficiency of unity. But in fact, the counterions remain diffusively distributed in a layer close to the surface and the charge efficiency of a (M)CDI cell is always below unity (Porada et al., 2013b). The GCS model assumes that the diffuse layer extending from one surface is not overlapping with that of a nearby surface. Nevertheless, in standard microporous (M)CDI electrodes, the pores where ions are primarily adsorbed (pore diameter < 2 nm) are much smaller than the EDL-thickness, and hence the EDLs are strongly overlapped (Porada et al., 2013b; Suss et al., 2015). A new EDL structure model termed modified Donnan (mD) model was developed in 2011 by Biesheuvel et al. (2011) to tackle the situation of fully overlapped EDLs. The mD-model assumes that EDLs lining the micropore walls are strongly overlapped, thereby leading to a relatively constant value of diffuse layer potential and ion concentration across the pore radius. The use of "modified" referred to two modifications of the classical Donnan approach, one by including a Stern layer in between the carbon matrix and the diffuse layer and the other by considering a non-electrostatic attraction (physi- or chemisorption) term for the ions transporting into the micropores in the absence of electronic charge (Porada et al., 2013b; Suss et al., 2015). A further improvement can be made to the mD-model when the salt concentration is higher than 40 mM, that is, making the non-electrostatic attraction inversely dependent on the total micropore ion concentration) (Biesheuvel et al., 2014; Kim et al., 2015).

The mD-model can be easily included in the porous electrode mass transport theory to relate the local potential drop across the EDLs to the local ion flux into the EDLs. The interplay between micro- and macro-scale transport mechanisms in the porous electrodes and bulk flow of a CDI unit dictates the ion concentration profile at the exit. For batch-mode operation, a one-dimensional transport model has been shown to work well in describing data sets for ion adsorption and charge storage in flow-by CDI cells as it can be assumed that, at every moment in time, the specific ion concentration within the electrode macropores is equal to that in the spacer channel, pipes and recycling reservoir (Porada et al., 2013b; Tang et al., 2015). For single-pass operation, a twodimensional transport model is required to quantify the dynamic ion electrosorption process (Hemmatifar et al., 2015; Tang et al., 2016a, b; Zhao et al., 2013b). In the water flow direction, the spacer channel needs to be divided into a certain number (M) of annular ideally-stirred volumes (or, sub-cells) in series with equal projected area. Under a constant-current charging, the electrodes should be discretized into M sequential sub-cells in the same manner, as shown in Fig. 9. In each of the M sub-cells, the current  $I_i$ 



Fig. 9. Schematic illustration of a plug flow model for ion transport and storage in the flow-by CDI cells under single-pass constant-current operation. Reproduced with permission from Tang et al. (2016a). Copyright 2016 American Chemical Society.

has the same value in the spacer channel, in the membrane and in the electrode, but this value differs between sub-cells and changes in time. According to previous studies, the two-dimensional transport model turns out to be a good approach in capturing the ion adsorption/desorption dynamics and predicting CDI performance over a range of operating conditions, cell arrangements and feed water compositions, not only for a monovalent salt (e.g., NaCl) solution but also for simple ionic mixtures (Tang et al., 2016a, b). For example, Tang et al. (2016a) investigated fluoride removal from brackish groundwaters by single-pass constant-current flow-by CDI and found that the developed relevant two-dimensional transport model provided a satisfactory reproduction of the effluent fluoride concentrations as a function of fluoride/chloride feed concentrations, adsorption current and pump flow rate, as shown in Fig. 10. Although the flow-by CDI device used in the work of Tang et al. (2016a) did not lower fluoride below the maximum permissible water quality levels, the studies described there enabled validation of a model that could subsequently be used to determine possible system configurations and operating conditions for realization of the target.

For classical CDI with unmodified electrodes, the ionic charge density in the EDLs of micropores exactly compensates the electronic charge in the carbon matrix, and the mD-model is applicable to this case. However, for chemically modified electrodes, modification to the mD-model is necessary. Biesheuvel et al. (2015) extended the mD-model by including an immobile chemical charge in the charge balance regarding flow-by CDI cells with fixed chemical charges within the micropores, and showed that the theory was able to capture and explain a variety of key features observed in experiments, including inverted operation, inversion peaks, and enhanced performance. Based on the work of Biesheuvel et al. (2015), He et al. (2018b) further incorporated the effect of variable chemical charges due to Faradaic reactions of redox-active species immobilized on the electrode surfaces. With respect to

electrode micropores containing acidic and basic surface groups that can protonate or deprotonate based on their individual equilibrium constants and the micropore and electrolyte pH environments, Hemmatifar et al. (2017) coupled the mD-model with the weak electrolyte acid-base equilibria theory with results demonstrating an excellent agreement between experiments and the new model.

Different from typical flow-by CDI cells where fluid flow and electric field are perpendicular generally necessitating a twodimensional model approach, the flow-through CDI cell is a cell design that can be well described by a one-dimensional model as the feed water flows straight through electrodes and parallel to the applied electric field direction. Up to now, a few models have been successfully developed to describe the ion adsorption/desorption dynamics and variation in electrical current in flow-through CDI cells, and has shown the value of modelling in elaborating the phenomena occurring in various scenarios which would otherwise be difficult to elucidate in any detail (Guyes et al., 2017a; Hawks et al., 2018; Qu et al., 2018). Ongoing research and efforts might make it come true to model other features important to flowthrough CDI cells, such as the effluent pH variations and the effects of chemical surface charge in porous electrodes.

Owing to the existence of IEMs, modelling the ion transport and storage in MCDI cells is more complicated than that in flow-by CDI cells. At the two membrane/solution interfaces there exists Donnan equilibrium, both on the edge of the membrane with the spacer channel and on the edge of the membrane with the macropores in the electrode. Within the IEMs, fixed charged groups are present with a high charge density, *X*. During transport, across the membrane both co-ion concentration and counterion concentration gradually change, but their difference remains equal to *X* due to electroneutrality in the membrane (Galama et al., 2013). By making some simplifications, for example, excluding transport of protons or hydroxyl-ions, assuming perfect symmetry in the cell, taking the



**Fig. 10**. Effluent F– concentration profiles during a single cycle for constant-current flow-by CDI under zero-volt desorption mode as a function of operating parameters: (a) F– feed concentration, (b) Cl– feed concentration, (c) adsorption current, and (d) pump flow rate. Symbols: experimental data; Lines: modelling results. Reproduced with permission from Tang et al. (2016a). Copyright 2016 American Chemical Society.

same diffusion coefficient for the cation and anion in the membrane, neglecting accumulation of ions in the membrane, setting zero water flow through the membrane, mathematical models for the MCDI processes based on a fully dissociated monovalent salt solution, like NaCl, could be established. These MCDI processes include desalination dynamics and performance over a wide range of possible design and operational scenarios (Suss et al., 2015; Zhao et al., 2013b). Though the MCDI community has covered some distance towards the ultimate goal of developing a robust model that confidently describes and predicts all possible data sets, the MCDI modelling is still in its infancy. Many questions remain with additional studies required to further improve our understanding of this technology. For example, the conditions examined in literature are a highly simplified subset of those likely to be experienced in treating real waters where a greater range of pH, a more extensive mixtures of ions and the presence of electrode fouling agents such as natural organic matter are to be expected. Transport modelling for mixtures of multiple ions in MCDI is still at an initial stage. No papers exist that describe the effects of membrane thickness or membrane charge density on the ion selective electrosorption.

#### 2.2. Flow-through capacitive deionization

With some modifications of a flow-by CDI cell, a cell named flow-through CDI could be developed in which the feed water flows straight through electrodes rather than between the electrodes, and parallel to the applied electric field direction (Cohen et al., 2011; Guyes et al., 2017a, 2017b; Hawks et al., 2018; Qu et al., 2018). The earliest work on flow-through CDI dates back to 1970 and was explored by Johnson et al. (1970). The following four decades saw little progress to flow-through CDI until Avraham et al. (2009) utilized flow-through electrodes in a three-electrode cell to attempt to improve the charge efficiency. One main advantage of flow-through CDI over flow-by CDI is that, since the separator does not act as a major channel for fluid flow, the separator thickness in the flow-through CDI may be minimized (from typically  $200-500\,\mu\text{m}$  to around  $10\,\mu\text{m}$ ) provided that no short circuit happens, thereby allowing for more compact cells, improved desalination rates and a higher reduction in salt concentration of the feed per unit of charge (Cohen et al., 2015; Guyes et al., 2017b; Suss et al., 2012). However, flow-through CDI cells suffer from greater feed pressures than flow-by CDI cells for the same throughput. In order to enable flowing through the electrodes at reasonable feed pressures, flow-through CDI cells generally require use of specialized electrode materials possessing relatively large macropores with diameters above 1 µm. For example, Suss et al. (2012) used hierarchical carbon aerogel monolith electrodes with macropore diameters of approximately 1 µm, while Cohen et al. (2011) used activated carbon fiber electrodes with  $100 \,\mu m$  gaps between fibers as the flow channels. In addition to the reduced feed pressures, it has to be noted that the electrodes should also possess nanometer-scale micropores enabling high salt adsorption. The requirement of both large macropores and small micropores seems to significantly limit the range of electrode materials suitable for flow-through operation. However, a recent work by Guyes et al. (2017b) has demonstrated that applying laser technique to perforate an array of channels with roughly 200 µm aperture diameters through the commercial CDI activated carbon electrodes could contribute to orders of magnitude improvement in the electrode hydraulic permeability without adverse influence on the electrodes' salt adsorption capacity or gravimetric capacitance, which implies that those electrode materials with high microporosity that are commonly employed in the flow-by CDI cells are likely to be tuned into attractive choices for flow-through electrodes. Another potential drawback of flow-through CDI cells is that oxidation of the positive electrodes occurs at a faster rate in flow-through CDI systems relative to flow-by CDI systems, though nitrogen sparging to eliminate dissolved oxygen in the feed water has been shown to extend the stability of flow-through CDI cells to a level comparable to flow-by CDI cells (Cohen et al., 2015; Guyes et al., 2017a, 2017b) and surface chemical treatments of carbon electrodes has been shown to enhance the charge efficiency in flow-through CDI processes (Cohen et al., 2011).

#### 2.3. Inverted capacitive deionization

Unsustainable CDI performance, mainly loss of salt separation, has been observed during CDI cycling operation under a constantvoltage charging mode (Bouhadana et al., 2011; Cohen et al., 2013). This performance degradation is primarily attributed to the formation of oxide (e.g., carboxylic groups) layers at the carbon surface via oxidation of the anode in an aqueous solution. These oxides lead to changes in the surface charge states including point of zero charge  $(pH_{PZC})$  and potential of zero charge  $(E_{PZC})$  (Cohen et al., 2013; Shapira et al., 2016). In order to sustain desalination performance, a novel CDI cell architecture, termed inverted capacitive deionization (i-CDI), was proposed by the research group of Gao et al. (2015b) in 2015. The i-CDI system involves the use of an anode with net negative surface charge and a cathode with net positive surface charge, and consequently shows a completely opposite adsorption-desorption behavior to the conventional CDI system with cell charging leading to ion desorption from the EDLs of the electrodes and cell discharging by short-circuiting the anode and cathode leading to ion adsorption (Fig. 11a and b) (Ovarzun et al., 2018).

Gao et al. (2015b) demonstrated the i-CDI concept via the use of pristine carbon xerogel with net positive surface charge as the cathode and modified carbon xerogel with net negative surface charge (containing carboxylic groups and oxidized silicon) as the anode. A significant enhancement in the performance stability and an increase of ~530% in lifetime were observed in the i-CDI system compared to a conventional CDI system operated under similar conditions due to the mitigation of carbon oxidation at the anode. In a more recent work, Gao et al. (2015a) constructed an i-CDI cell using an amine-treated cathode (with -NH<sub>3</sub><sup>+</sup> groups providing net positive surface charge) and an acid-treated anode (with -COO<sup>-</sup> groups providing net negative surface charge). In comparison to the previous i-CDI cell where a salt removal capacity of ~1.7 mg  $g^{-1}$  was achieved at a maximum working voltage of 0.8/0V, this i-CDI cell could offer a salt removal capacity of ~5.3 mg  $g^{-1}$  at a maximum working voltage of 1.1/0 V, representing a significant improvement with regard to both salt removal capacity and working voltage window. Wu et al. (2016) further assembled an i-CDI cell equipped with a quaternized poly (4-vinylpyridine) modified activated carbon cathode and a nitric acid treated activated carbon anode and the cell exhibited excellent i-CDI performance. The working voltage window of the i-CDI cell could reach 1.4 V and its salt removal capacity could be as high as  $9.6 \text{ mg g}^{-1}$ . Instead of synthesizing new carbon electrodes to expand the working voltage window, Gao et al. (2018) developed a novel i-CDI operational mode to improve the desalination performance. In the conventional i-CDI operational mode, i.e.,  $V_{charge} = 0.8 \text{ V}$  and  $V_{discharge} = 0 \text{ V} (0.8/0 \text{ V})$ , the i-CDI cell exhibited a salt adsorption capacity (SAC) of 6.0  $\pm$  0.8 mg g  $^{-1}$  with a stable salt separation lasting approximately 409 h. In the novel i-CDI operational mode (0.4/-0.4 V), it was found that not only was the separation process stabilized up to approximately 420 h but the SAC also increased to  $7.2 \pm 0.3 \text{ mg g}^{-1}$ . Furthermore, more stable pH and dissolved oxygen (DO) responses were observed at 0.4/-0.4 V compared to 0.8/0V. A reasonable explanation for such an



**Fig. 11.** (a) Schematic of i-CDI cell which features nitrate regeneration. Negative electrode (CTA-AC) is treated with cetrimonium bromide (CTAB) and positive electrode (DBS-AC) with sodium dodecyl benzene sulphonate (SDBS). The external voltage forces electrons to flow from DBS-AC to CTA-AC, repelling Na+ and NO3- ions from their respective electrodes. Reproduced with permission from Oyarzun et al. (2018). Copyright 2018 Elsevier. (b) Schematic of short circuit adsorption process. Na+ and NO3- ions are adsorbed, forcing migration of electrons from CTA-AC to DBS-AC. Reproduced with permission from Oyarzun et al. (2018). Copyright 2018 Elsevier. (c) Schematic of short circuit adsorption process. Na+ and NO3- ions are adsorbed, forcing migration of electrons from CTA-AC to DBS-AC. Reproduced with permission from Oyarzun et al. (2018). Copyright 2018 Elsevier. (c) Schematic of the working voltage window for the i-CDI. E+ and E- represent the potentials distributed at the anode and cathode, respectively. E0 represents the short-circuit potential. Adapted with permission from Gao et al. (2015b). Copyright 2015 Royal Society of Chemistry.

improved performance was that the reduced  $V_{charge}$  mitigated carbon oxidation at the anode and DO reduction at the cathode while the reduced  $V_{discharge}$  compensated for SAC (Gao et al., 2018). Most recently, Oyarzun et al. (2018) presented an i-CDI cell for nitrate removal with the cell fabricated with an activated carbon cathode modified by cetrimonium bromide and an activated carbon anode modified by sodium dodecyl benzene sulphonate. It turned out that a successful nitrate removal (up to more than 10 mg NaNO<sub>3</sub> per g of both electrodes) was achieved with this i-CDI system, suggesting that functionalized i-CDI systems might have great potential for ionic pollutant removal.

Inverted CDI features excellent operation longevity but lacks substantial salt removal capacity which is mainly limited by its relatively small working voltage window. The i-CDI working voltage window is regulated by the difference between  $E_{PZC}$  of anode and E<sub>PZC</sub> of cathode, as shown in Fig. 11c. Therefore, optimizing the  $E_{PZC}$  of electrodes (specifically, the anode needs a more positive  $E_{PZC}$  whereas the cathode requires a more negative  $E_{PZC}$ ) to enlarge the working voltage window of i-CDI is of great importance. Generally, introduction of negatively charged functional groups can shift  $E_{PZC}$  to a more positive value while introduction of positively charged functional groups shifts *E*<sub>PZC</sub> to a more negative value (Wu et al., 2016). In i-CDI systems, oxidation of the anode is not regarded as an adverse effect as is the case in conventional CDI systems. In fact, oxygen-containing functional groups formed during carbon oxidation increase the net negative surface charge and shift  $E_{PZC}$  of the anode to a more positive value, thereby favorably contributing to the expansion of the intrinsic working voltage window. However, it is worth mentioning here that the continued formation of oxide layers at the surface of anode might result in an increase in the resistance of the anode, whereby this layer eventually suppresses ionic storage in the i-CDI cell causing performance degradation (Gao et al., 2018).

#### 2.4. Flow-electrode capacitive deionization

For conventional (M)CDI cells, salt removal capacity is largely constrained by the fixed electrodes, making conventional (M)CDI only suitable for treating brackish/low-salinity water. In addition, preparation of the fixed electrodes is kind of complicated and approximately 20% of the fabricated electrodes is made up of conductive agents (e.g., carbon black) and polymer binder (e.g., polytetrafluoroethylene) that have negligible ion adsorption capacity. Apart from adding dead mass, the presence of polymer binder may also block a large amount of pore volume of the active carbon particles (Suss et al., 2015). Moreover, conventional (M)CDI systems operate in an intermittent manner with a deionization period (freshwater produced) followed by a regeneration period (wastewater produced). In view of these limitations of conventional (M)CDI systems, leon et al. (2013) pioneered the use of flowing electrodes and designed an innovative CDI cell architecture termed flow-electrode capacitive deionization (FCDI) to improve the performance of (M)CDI. As shown in Figs. 2e and 12a, typical FCDI cell geometry is similar to that of MCDI except for the electrode part. In contrast to MCDI using the fixed electrode between current collectors and IEMs, FCDI employs the aqueous suspensions of carbon particles flowing through a serpentine channel carved on the current collector. When an electrical voltage is applied between the two current collectors of an FCDI cell, ions present in the feed water would migrate through IEMs and enter the flow-electrode, where they would be eventually adsorbed on the suspended carbon material or dissolved in the aqueous phase of the flow-electrodes with cations concentrated in the cathode chamber and anions concentrated in the anode chamber (Jeon et al., 2013; Moreno and Hatzell, 2018; Nativ et al., 2017; Yang et al., 2017b). Representative of an electrodialytical desalination mechanism, the proportion of ions accumulated in the aqueous phase of the flow-electrodes increases



**Fig. 12.** Schematic illustration of (a) a typical FCDI cell geometry, (b) the continuous inflow of fresh carbon electrodes and continuous production of the desalinated water with electrode regeneration completed downstream of the cell by simply mixing the positive and negative carbon slurries followed by carbon separation from water via settling, and (c) a continuous FCDI desalination system comprising only one module and one flow-electrode. The sub-figure (a) is adapted with permission from Zhang et al. (2018b), Copyright 2018 American Chemical Society and the sub-figure (c) is reproduced with permission from Rommerskirchen et al. (2015), Copyright 2015 Elsevier.

with intensified Faradaic reactions producing  $H^+$  (anode chamber) and  $OH^-$  (cathode chamber) (Ma et al., 2018; Nativ et al., 2017).

On the basis of continuous inflow of fresh carbon electrodes, FCDI exhibits an excellent desalting efficiency in a highconcentration NaCl solution attributed to the infinite ion adsorption capacity of the flow-electrode as compared to the limited capacity of the static electrode used in conventional (M)CDI (Doornbusch et al., 2016; Jeon et al., 2013). Meanwhile, FCDI enables a continuous desalinating behavior in the unit cell and steadily produces desalted water with electrode regeneration completed downstream of the cell by simply mixing the positive and negative carbon slurries followed by carbon separation from water via settling (Jeon et al., 2013, 2014; Yang et al., 2016a). The two important features are visually described in Fig. 12b. Studies related to FCDI under such an operational mode indicated that the effluent NaCl concentration would decrease rapidly and then reach a plateau (Jeon et al., 2013). In contrast, when a conventional (M) CDI cell is used, the effluent NaCl concentration would decrease rapidly and then increase and finally return to its original value as ion adsorption on the fixed electrodes reaches equilibrium (Porada et al., 2013b).

Since FCDI was proposed in 2013, FCDI has attracted many researchers' interest. Studies aimed at enhancing FCDI performance and achieving a cost-effective FCDI system have been performed in various aspects, mainly including:

(1) Flow-electrode. As flow-electrode is the key element of FCDI. extensive efforts have been made to optimize the carbon materials and aqueous electrolyte constituting the flowelectrode. For instance, Hatzell et al. (2015) modified granular AC with nitric acid to increase the oxygen-containing surface functional groups and then used the oxidized AC for flow electrodes. It was found that chemical oxidation of AC was favorable to reducing the viscosity of carbon suspension, and resultantly a higher carbon content could be used without increasing pumping energy when using oxidized AC while the increased carbon loading contributed to a decrease in the deionization energy consumption and an increase in salt removal efficiency. Similarly, Park et al. (2016) prepared surface-modified AC suspensions (AC coated with trimethylammonium for flow-anode and AC coated with sulfonate for flow-cathode) to achieve a higher carbon loading without sacrificing the flowability (viscosity). Considering the excellent conductivity of carbon black facilitating charge transfer, Liang et al. (2017) added a certain dosage of carbon black with an average diameter of  $12\,\mu m$ into the AC flow electrodes, leading to a decrease in the FCDI's internal resistance and consequently an improved charge efficiency. Ma et al. (2016b) developed redox-active flow electrodes by adding 14 mM hydroquinone to 1 wt% activated charcoal suspension and demonstrated that the presence of aqueous hydroquinone/benzoquinone couple in flow electrodes enhanced electron transfer significantly and facilitated both salt adsorption and desorption processes as a result of the facile redox transformation between hydroquinone and benzoquinone. Yang et al. (2016a) fabricated flowelectrodes using an aqueous electrolyte with a high salt concentration (2.44 wt%) and confirmed that this method was effective to reduce the internal resistance of the electrode chambers and improve FCDI's desalting efficiency, thereby successfully overcoming the limitations of flowelectrodes using low concentrated salt water as an electrolyte for the use of FCDI. Doornbusch et al. (2016) developed a FCDI system leveraging upflow fluidized bed electrodes and showed that the carbon loading in the flow electrode could reach 35 wt% while maintaining flowability, which promised more effective electric charge percolation through the electrode than previously used flow electrodes (maximum carbon loading 20 wt%). Cohen et al. (2016) introduced a novel class of suspension electrodes combining dilute slurries and dense upflow fluidized beds with results showing that a synergetic effect could be achieved in the enhancement of electrode electronic conductivity when adding dilute slurry to dense fluidized bed. Xu et al. (2016) proposed an asymmetric FCDI system by using activated carbon (AC)/MnO<sub>2</sub> suspension as the anode and AC suspension as the cathode so as to improve the operation voltage to 1.8 V, thereby achieving a much higher salt removal efficiency than conventional FCDI.

(2) Cell design. To maximize the advantages of FCDI, lower FCDI's construction investment and operation costs, and simply the FCDI cell system for facile scale-up, several research groups have focused efforts on improving the FCDI cell design. Gendel et al. (2014) developed a truly continuous FCDI process where water desalination, brine production and electrode regeneration were all performed continuously and simultaneously. The feed water is split between two FCDI cells with the same configuration but with reversed potential. Both carbon slurries are continuously recirculated between the two FCDI modules (one producing desalinated stream and the other producing concentrated stream). However, this system suffers from high energy consumption originated from application of a voltage for water desalination in the first module and additionally for electrode regeneration in the second module, as well as the circulation pumping of two flow-electrodes. Following this work, Rommerskirchen et al. (2015) further designed a continuous FCDI system that comprised only one module and one flowelectrode performing the same function as that introduced by Gendel et al. (2014) (see Fig. 12c). The single flowelectrode and single module FCDI desalination system is beneficial to reducing energy and investment costs and lowering the threshold to a large-scale implementation. In the majority of FCDI cell architectures, the flow electrodes are separated from the feed water channel by IEMs, as shown in Figs. 2e and 12a. Yet Hatzell et al. (2014a) proposed a membrane-free FCDI configuration that could potentially develop into a low-cost system. Specifically, two flowelectrodes prepared by mixing sea or brackish water with activated carbon flow through electrode compartments with a porous separator in-between. At the end of electrode compartments, charged carbon particles carrying counterions are sieved via the use of polymeric or non-woven glass fibers to produce desalinated water. After sieving, the carbon can be flushed in a high concentration stream, discharged and recycled for further use. In an effort to simplify the FCDI cell system, Lee et al. (2018c) combined the spacer and IEMs into a single unit by coating the IEMs (17 wt% poly(phenylene oxide) in N-methyl-2-pyrrolidone as AEM solution and 20 wt % poly(phenylene oxide) in dimethylacetamide as CEM solution) on the surface of a porous ceramic structure acting as the spacer. This combination avoids the use of costly freestanding IEMs and makes FCDI cells readily scaled up. Recently, as a ground-breaking design, a highly compact and scalable three-dimensional (3D) FCDI system was realized by utilizing honeycomb-shaped porous lattice scaffolds and by coating an IEM (AEM or CEM solution) and a graphene layer within appropriate channels, as shown in Fig. 13 (Cho et al., 2017). The 3D FCDI system does not require the waterchannel spacer layer, free-standing IEMs and thick current



**Fig. 13.** Schematic diagram of the highly compact and scalable three-dimensional (3D) FCDI system based on honeycomb-shaped porous lattice scaffolds made out of cordierite: (a) top-view ( $1 \times 3$ -channel cell), (b)  $3 \times 3$ -channel cell and (c) desalination process. Once applying a voltage, Na+ and Cl- from the saline feed water flowing through a water-channel can be transported through micro-scale pores in the cordierite. Then, the ions cross-flow through IEMs selectively and are adsorbed onto suspended carbon materials in the flow-electrodes. (d) Variation in salt concentration of  $1 \times 3$ - and  $3 \times 3$ -channel cells during desalination operated in the batch mode. Adapted with permission from Cho et al. (2017). Copyright 2017 Royal Society of Chemistry.

collectors, which makes the size of each cell much smaller and more compact than typical FCDI cells thereby allowing for a high volumetric efficiency. Moreover, the unit cell can be scaled-up readily in three dimensions and the desalination efficiency and capacity significantly increase as the cell size or number is extended (see Fig. 13).

(3) Energy harvesting. Harvesting/recovering energy to minimize the overall energy consumption of FCDI system is another important aspect. It has been reported that, during constant-current discharge, approximately 20% of the supplied energy in a FCDI cell charged by constant-voltage could be recovered by energy extraction using an external circuit when the ions stored in the flow-electrodes are released into salt water (Jeon et al., 2014). Furthermore, it has been demonstrated that using a flow-electrode system for continuous energy harvesting is feasible via capacitive mixing from naturally available differences in water salinity (see Fig. 14) and concentration differences in bicarbonate ions  $(HCO_3^-)$  dissolved in water from the exhaust gases of a power plant with high levels of CO<sub>2</sub> versus the low CO<sub>2</sub> concentration in air (see Fig. 15) (Hatzell et al., 2014b; Porada et al., 2014), which provides a new platform for harvesting energy and has the potential to impact on the fields of energy and water technology.

Also of note is that FCDI systems can be integrated with other technologies to provide synergy towards desalination. One example is combining FCDI with neutralization dialysis (ND) to fabricate a cell named capacitive neutralization deionization with flow electrodes (FCND) (Wang et al., 2016). The only difference between FCDI and FCND is that the acidic (e.g., HCI) and the alkaline (e.g., NaOH) solutions are used in the flow-electrode channels in place of salt solutions. In FCND cells, capacitive adsorption of salt ions occurs simultaneously during the neutralization dialysis



**Fig. 14.** (a) Flow-electrode capacitive mixing (CapMix) based on an energy extraction process using four separate reactors. (A) Flow electrodes are spontaneously charged using high-concentration (HC) solution in the middle chamber, so that energy is harvested. (B) The flow electrodes equilibrate to the membrane potential established with low-concentration (LC) solution in the middle chamber under open circuit conditions. (C) Energy is again harvested through an external load. (D) The flow electrodes equilibrate to the HC solution under open circuit conditions. (b) Contour plot showing expected energy (J) extracted from capacitive electrode with respect to the voltage and capacitance of the material. Start indicates the potential energy extracted from CapMix system operated at low voltages. Adapted with permission from Hatzell et al. (2014b). Published by American Chemical Society.



Flat plate and cylindrical ion exchange membranes for energy

Fig. 15. Schematic view of (A) cylindrical and (B) flat plate ion-exchange membranes used for continuous energy production from capacitive mixing associated with CO2 emissions and from differences in water salinity. (C) Picture of continuous system utilizing cylindrical ion-exchange membranes for energy production. Adapted with permission from Porada et al. (2014). Published by The Royal Society of Chemistry.

process, which makes FCND perform better than individual FCDI or ND in terms of average salt adsorption rate and salt removal efficiency. A second example is coupling FCDI with nanofiltration (NF) with an energy-efficient hybrid desalination process achieved with tunable salt rejection and high water recovery for high-salinity brackish water (~10000 mg  $L^{-1}$  NaCl) (Choi et al., 2017). It turned out that the hybrid FCDI-NF system provided ~20% energy saving compared to the best reported energy consumption of a brackish water reverse osmosis unit.

Beyond the application of brackish and sea water desalination, FCDI has also been investigated for other applications (Fang et al., 2018; He et al., 2018a; Linnartz et al., 2017; Nativ et al., 2018; Yang et al., 2016b; Zhang et al., 2018b). For example, FCDI operated in short-circuited closed-cycle mode was found to be a costeffective technology for brackish water softening with the charge neutralization achieved by continuous mixing of the carbon particles significantly inhibiting scale formation on the electrode surface (He et al., 2018a). FCDI for a salt metathesis process was



Fig. 16. Combination of a FCDI unit with a hydrophobic gas-permeable hollow fiber membrane contactor and the use of the hybrid system for removal and recovery of ammonium (NH4+) from dilute wastewaters. Reproduced with permission from Zhang et al. (2018b). Copyright 2018 American Chemical Society.

demonstrated by Linnartz et al. (2017) where four identical FCDI cells were used to generate a concentrated valuable magnesium sulfate (MgSO<sub>4</sub>) solution from dilute MgCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> (or  $K_2SO_4$ ) solutions. Further, FCDI systems have been employed as a method for the recovery of valuable chemicals from low-strength wastewaters (Fang et al., 2018; Zhang et al., 2018b). Zhang et al. (2018b) combined a FCDI unit with a hydrophobic gas-permeable hollow fiber membrane contactor and used the hybrid system for removal and recovery of ammonium  $(NH_4^+)$  from dilute wastewaters. During operation, NH<sub>4</sub><sup>+</sup> migrates across the CEM and accumulates in the FCDI cathode chamber where alkaline environment favors the conversion of  $NH_4^+$  to dissolved  $NH_3(aq)$  followed by a production of NH<sub>3</sub>(g) (Ma et al., 2016b; Nativ et al., 2017; Zhang et al., 2018b).  $NH_3(g)$  will readily diffuse through the gas-permeable membrane into an acid solution and be recovered as an ammonium salt that can potentially be marketed as a fertilizer, as shown in Fig. 16.

#### 3. Cells with battery electrodes

#### 3.1. Hybrid capacitive deionization

(M)CDI is highlighted as a desalination technology in which ions are harvested and stored in the electric double layers of capacitive electrodes. The ion removal capacity of (M)CDI systems is somewhat limited and thus not sufficient for desalting highconcentration saline water. Meanwhile, the energy consumption of (M)CDI systems for treating high-salinity water significantly exceeds the energy required for reverse osmosis systems (Srimuk et al., 2017a). Consequently, an important task for current research is to overcome the intrinsic limitations of (M)CDI for brackish water and make the technology accessible to higher molar concentrations. Inspired from the burgeoning field of energy storage such as lithium ion batteries and sodium ion batteries, a highly promising approach is to replace one of the two capacitive electrodes with a battery (i.e., Faradaic) electrode with this novel desalination technique referred to as hybrid capacitive deionization (HCDI). The typical HCDI cell architecture is shown in Fig. 2f, and AEM is not required in some cases (Srimuk et al., 2017b). Apart from being able to reduce energy consumption and avoid parasitic reactions through the use of a smaller voltage window, battery electrodes could offer a higher specific capacity than capacitive electrodes since ions are not just absorbed on the surface of battery electrodes but also being intercalated into their crystal structures via chemical bonds (Guo et al., 2018; Lee et al., 2014; Suss and Presser, 2018). Normally, a sodium battery electrode instead of a chloride battery electrode is employed because materials for sodium-ion Faradaic intercalation/de-intercalation are diverse and have been intensively investigated while materials for chloride-ion Faradaic intercalation are limited.

Lee et al. (2014) first introduced the concept of HCDI in 2014 with the HCDI cell composed of a Na<sub>4</sub>Mn<sub>9</sub>O<sub>18</sub> (a representative positive-electrode material for sodium ion batteries) electrode as the cathode, a porous activated carbon electrode as the anode and an AEM placed adjacent to the carbon electrode. Prior to desalination tests, a certain voltage (vs. Ag/AgCl) needed to be applied to the Na<sub>4</sub>Mn<sub>9</sub>O<sub>18</sub> electrode for an appropriate duration of time to extract  $Na^+$  ( $Na_4Mn_9O_{18} \rightarrow Na_{4-9x}Mn_9O_{18} + 9xNa^+ + 9xe^-$ ). Desalination process was initiated by applying a positive voltage with the result that Na<sup>+</sup> was intercalated into Na<sub>4</sub>Mn<sub>9</sub>O<sub>18</sub> electrode chemical via reactions  $(Na_{4-9x}Mn_{9}O_{18} +$  $9xNa^+ +$  $9xe^- \rightarrow Na_4Mn_9O_{18}$ ) while Cl<sup>-</sup> was physically adsorbed in the electric double layers formed at the surface of porous carbon electrode. Reversely, desorption process occurred by applying a negative voltage to release the captured ions. The HCDI system exhibited more than double the salt removal sorption capacity  $(31.2 \text{ mg g}^{-1})$  than a conventional CDI system  $(13.5 \text{ mg g}^{-1})$  and revealed a rapid ion removal rate and excellent stability. successfully demonstrating its superior deionization performance.

Besides  $Na_4Mn_9O_{18}$ , other  $Na^+$  Faradaic electrodes such as  $Na_2FeP_2O_7$  (Kim et al., 2016b),  $NaTi_2(PO_4)_3$  (Huang et al., 2017b) and Prussian blue (PB) (Guo et al., 2017) have also been explored, and it was found that pairing these  $Na^+$  battery electrodes with a capacitive activated carbon as a HCDI cell also led to significantly improved salt adsorption capacity compared to that of traditional (M)CDI cells. Fig. 17 summarizes the materials that have been reported to exhibit reversible sodium-ion Faradaic insertion/release in sodium-ion batteries within the decomposition voltage of water (Chihara et al., 2012; Deng et al., 2014; Guo et al., 2017; Jung et al., 2014; Kim et al., 2012b, 2016b; Liu et al., 2016b; Palomares et al., 2012; Park et al., 2011b; Senguttuvan et al., 2011; Song et al., 2011;



**Fig. 17.** Plot of potential (V vs. SHE) versus specific capacity for materials that have been reported to exhibit reversible sodium-ion Faradaic insertion/release in sodium-ion batteries within the decomposition voltage of water, that is, the potential materials that may be applied in HCDI, desalination battery and CID cells.

2014; Su and Wang, 2013; Wang et al., 2015b; Whitacre et al., 2010; Wu et al., 2015b, 2018; Yu et al., 2015; Zhao et al., 2013a; Zhu et al., 2013, 2017), that is, the potential materials that may be applied in HCDI. Generally, materials with higher specific capacity (mAh  $g^{-1}$ ) are expected to store a greater amount of charge and thus provide a larger SAC. Here, it is worth noting that, in addition to the pursuit of a large SAC, other factors should be also considered. For example, the poor electrical conductivity and relatively high capital cost of Na<sup>+</sup> battery electrode materials hinder the advancement of HCDI to some degree. To address this issue, an effective method is to synthesize the composite of carbon and Na<sup>+</sup> battery electrode materials with both characteristics of a battery and a capacitor. Specifically, depositing thin layers of MnO<sub>2</sub> onto carbon substrates provides an efficient alternative to bulk Na<sup>+</sup> insertion materials (i.e., MnO<sub>2</sub>) by preserving the rich internal pore structures and excellent electrical conductivity of the carbon substrate while minimizing the Mn mass required to achieve increased capacity and cation selectivity (Hand and Cusick, 2017). Apart from the benefits of resolving low electrical conductivity and reducing capital cost of bulk Na<sup>+</sup> insertion/de-insertion materials, it was reported that utilizing the composite of carbon and Na<sup>+</sup> battery electrode materials also contributes to an improved cycling performance (Divyapriya et al., 2018; Huang et al., 2017b; Zhou et al., 2018).

Representing an inverted version of the typical HCDI cells, Yoon et al. (2017) constructed a HCDI cell consisting of a chloride battery electrode (anode), a capacitive carbon electrode (cathode) and a CEM. The chloride battery electrode was fabricated by coating a small amount of Ag onto a capacitive carbon electrode via photo-induced reduction reaction. Compared to the CDI cell assembled with a pair of capacitive carbon electrodes and one CEM, the Ag coated HCDI cell led to an significant improvement in the deionization capacity (88% more), maximum deionization rate (39% more) and charge efficiency (76%  $\rightarrow$  92%), which could be explained by the enhanced specific capacity combining the capacitance of carbon electrode and Ag mediated charge transfer reaction (Ag + Cl<sup>-</sup>  $\Rightarrow$  AgCl + e<sup>-</sup>). Moreover, the Ag coated HCDI was found to be superior to the MCDI in terms of energy consumption.

#### 3.2. Desalination battery

Unlike a HCDI cell combing a battery electrode (e.g., sodium manganese oxide) and a capacitive electrode (e.g., porous carbon), a desalination battery cell is composed of two different battery electrodes (one for cation Faradaic intercalation/de-intercalation and the other for anion Faradaic intercalation/de-intercalation) (Fig. 2h). IEMs could be placed in front of each electrode to enhance performance by blocking the co-ions during the capture/ release process. Generally, a constant current instead of a constant voltage is applied for both desalination and salination steps, and the charging/discharging process is performed until the cell voltage reaches a pre-determined value. In desalination battery systems, the unit  $F g^{-1}$  employed to describe the capacitance of capacitive materials becomes useless and the unit mAh  $g^{-1}$  employed to represent the specific capacity of battery materials should be adopted since charge and cell voltage are no longer behaving like those in a capacitor.

The concept of desalination battery was first proposed and demonstrated by Pasta et al. (2012) with the cell consisting of a Ag negative electrode and a Na<sub>2</sub>Mn<sub>5</sub>O<sub>10</sub> positive electrode. Tests were conducted in a static 300  $\mu$ L electrolyte. The desalination cycle is started with charging the electrodes in the absence of mobile sodium and chloride ions, rendering Na<sub>2</sub>Mn<sub>5</sub>O<sub>10</sub> oxidized into MnO<sub>2</sub>. During the desalination cycle, Cl<sup>-</sup> is chemically captured from the electrolyte to the silver electrode forming AgCl (Eq. (1)) while Na<sup>+</sup> is chemically intercalated in the bulk of MnO<sub>2</sub> electrode forming  $Na_2Mn_5O_{10}$  (Eq. (2)). The reverse process will happen during the desorption cycle as shown in Eq. (3) and Eq. (4). Specifically, a complete cycle of the  $Ag-Na_2Mn_5O_{10}$  system includes four steps: 1) Fully charged electrodes are immersed in seawater. Desalination occurs by applying a negative constant current; 2) Removal of the desalinated water and replenishment of new seawater: 3) Releasing the ions incorporated in the first step and creating concentrated seawater by applying a positive constant current; 4) Replacing the concentrated seawater with new seawater, and the system is ready for the next cycle. A low energy consumption of 0.29 kWh  $m^{-3}$  for the desalination process (removal of 25% salt) was achieved using this novel cell design and fast exchange of ions between the solid and the liquid phase occurred. Na<sup>+</sup> and Cl<sup>-</sup> could potentially be selectively removed. However, in spite of a landmark study, there was no report about the adsorption capacity of the electrodes and only one cycle was carried out in the Ag-Na<sub>2</sub>Mn<sub>5</sub>O<sub>10</sub> system with the cycle repeatability unknown. In addition, oxidation of Na<sub>2</sub>Mn<sub>5</sub>O<sub>10</sub> to MnO<sub>2</sub> prior to desalination cycle resulted in noticeable polarization causing a decreased capacity.

Adsorption process: 
$$Ag + Cl^- \rightarrow AgCl + e^-$$
 (1)

$$5MnO_2 + 2Na^+ + 2e^- \to Na_2Mn_5O_{10}$$
 (2)

Desorption process:  $AgCl + e^- \rightarrow Ag + Cl^-$  (3)

$$Na_2Mn_5O_{10} \rightarrow 5MnO_2 + 2Na^+ + 2e^-$$
 (4)

Overall reaction: 
$$5MnO_2 + 2Ag + 2NaCl \leftrightarrow Na_2Mn_5O_{10} + 2AgCl$$
 (5)

Based on the pioneer work of Pasta et al. (2012), Chen et al. (2017a) advanced the dual-ion electrochemistry deionization system by using AgCl as the negative electrode, Na<sub>0.44</sub>MnO<sub>2</sub> as the positive electrode and flowing NaCl solution as the electrolyte. Feed NaCl solution was pumped through the AgCl-Na<sub>0.44</sub>MnO<sub>2</sub> deionization device and then flowed back. When a positive current is applied, Cl<sup>-</sup> is electrochemically released from the AgCl electrode  $(AgCl + e^- \rightarrow Ag + Cl^-)$  while  $Na^+$  is electrochemically deintercalated from the Na<sub>0.44</sub>MnO<sub>2</sub> electrode  $(Na_{0.44}MnO_2 \rightarrow Na_{0.44-x}MnO_2 + xNa^+ + xe^-)$  to the flow electrolyte. When switching to negative current, Na<sup>+</sup> and Cl<sup>-</sup> are extracted from the flow electrolyte to their corresponding electrodes undergoing the reverse redox reactions. Through 100 cycling tests, the AgCl-Na<sub>0.44</sub>MnO<sub>2</sub> system was found to possess a stable and reversible salt adsorption capacity of  $57.4 \text{ mg g}^{-1}$  at  $100 \text{ mA g}^{-1}$ current density, which is much higher than that obtained by traditional or hybrid CDI device. The average charge efficiency is high, up to 0.979/0.956 during the salt desorption/adsorption process. In another study by Kim et al. (2017c), selective Na<sup>+</sup> separation from a solution containing diverse cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) using the AgCl-Na<sub>0.44</sub>MnO<sub>2</sub> system was investigated with experimental results indicating that, in an electrolyte where the cations had equal molar concentrations, the selectivity toward Na<sup>+</sup> was over 13 times higher than K<sup>+</sup>, and 6–8 times higher than  $Ca^{2+}$  and  $Mg^{2+}$ .

With respect to Cl<sup>-</sup> capturing/intercalation electrode material, silver shows several advantages: stability of potential, corrosion resistance and bactericidal properties (Pasta et al., 2012). Nevertheless, high cost of Ag (553 USD kg<sup>-1</sup>) and poor electrical conductivity of AgCl will limit the usage of Ag/AgCl electrode in practical and large-scale desalination battery cells. As such, seeking a sustainable, efficient and economical Cl-storage electrode is of

considerable importance. Bi/BiOCl electrode, a recently discovered cost-effective (9.8 USD kg<sup>-1</sup> for Bi) and stable (insoluble in a wide pH and potential range) Cl<sup>-</sup> capture/release electrode, opens up new possibilities for electrochemical Cl<sup>-</sup> removal or desalination applications. Chen et al. (2017b) carried out a similar study to their previous work (Chen et al., 2017a) by replacing AgCl electrode with BiOCl electrode while keeping Na<sup>+</sup> intercalation electrode material unchanged with this modification contributing to an enhancement in salt adsorption capacity from 57.4 mg g<sup>-1</sup> to 68.5 mg g<sup>-1</sup>. The redox reactions occurred during salt desorption and adsorption processes in the BiOCl–Na<sub>0.44</sub>MnO<sub>2</sub> system are described as follows,

Desorption process:  $3BiOCl + 3e^- \rightarrow Bi + Bi_2O_3 + 3Cl^-$  (6)

$$Na_{0.44}MnO_2 \rightarrow Na_{0.44-x}MnO_2 + xNa^+ + xe^-$$
 (7)

Adsorption process:  $Bi + Bi_2O_3 + 3Cl^- \rightarrow 3BiOCl + 3e^-$  (8)

$$Na_{0.44-x}MnO_2 + xNa^+ + xe^- \rightarrow Na_{0.44}MnO_2$$
(9)

Overall reaction:

$$\begin{aligned} &3xBiOCl + 3Na_{0.44}MnO_2 \leftrightarrow xBi + xBi_2O_3 + 3Na_{0.44-x}MnO_2 \\ &+ 3xNaCl \end{aligned}$$

(10)

Interestingly, when Bi is employed as the Cl-storage positive electrode, the electrochemical reaction involving its conversion to BiOCl is significantly different from that shown in Eq. (8) (Nam and Choi, 2017). For example, in a desalination battery cell composed of a Bi positive electrode and a  $NaTi_2(PO_4)_3$  negative electrode, desalination happens as a result of the following electrochemical reactions (Nam and Choi, 2017),

$$Bi + Cl^{-} + H_2 O \rightarrow BiOCl + 2H^{+} + 3e^{-}$$
 (11)

$$NaTi_{2}(PO_{4})_{3} + 2Na^{+} + 2e^{-} \rightarrow Na_{3}Ti_{2}(PO_{4})_{3}$$
 (12)

Overall reaction:

$$3/2NaTi_2(PO_4)_3 + Bi + 3Na^+ + Cl^- + H_2O \rightarrow 3/2Na_3Ti_2(PO_4)_3 + BiOCl + 2H^+$$
  
(13)

Normally, new seawater (pH neutral) is used as feedwater for desorption process. However, in this case, the kinetics of Cl<sup>-</sup> release from BiOCl would be slow as protons are needed to facilitate reduction of BiOCl to Bi by serving as oxygen acceptors (BiOCl +  $2H^+ + 3e^- \rightarrow Bi + Cl^- + H_2O$ ). It was suggested to address this issue by the use of an acidic solution (70 mM HCl) during desorption since battery electrodes used in batch-mode tests can be lifted out of the desalinated water after desalination and immersed into a different solution for desorption. Another possible drawback of the Bi/NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> system is an imbalance in Na<sup>+</sup> and Cl<sup>-</sup> storage. As can be seen from Eq. (13), the molar ratio of Na<sup>+</sup> and Cl<sup>-</sup> stored in the Bi/NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> cell during desalination is 3:1 rather than 1:1, which indicates that, when Na<sup>+</sup> in the seawater is completely removed, two thirds of Cl<sup>-</sup> would still remain in the solution with charge neutralized by H<sup>+</sup> produced during the transformation of Bi to BiOCl. A solution to this issue was proposed, i.e., adopting a hydrogen evolution electrode to replace the NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> electrode to perform reduction of H<sup>+</sup> to H<sub>2</sub> while Bi electrode finishes removing the remaining Cl<sup>-</sup>.

A promising desalination battery design is expected to possess

properties of operational convenience, low cost, low energy consumption, high ion removal capacity and performance stability. Among the desalination battery cells developed so far, the BiO-Cl–Na<sub>0.44</sub>MnO<sub>2</sub> cell appears to be the most practical. However, in order to render desalination battery a truly feasible method for seawater desalination, development of better combinations of Clstorage battery electrode and Na-storage battery electrode is still required and deserves continuing research input. Discovering new Cl<sup>-</sup> or Na<sup>+</sup> capturing/intercalation electrode material and synthesizing composite electrodes via the use of existing materials to achieve synergistic effects (e.g., incorporation of AgCl into porous carbonaceous materials to overcome the disadvantage of poor electrical conductivity of AgCl) represent two important research directions.

#### 3.3. Cation intercalation desalination

As previously described, in cells of HCDI and desalination battery, a Na<sup>+</sup>-intercalation battery electrode is paired with a different electrode for Cl<sup>-</sup> adsorption, either a capacitive electrode or an Cl<sup>-</sup>intercalation battery electrode. Considering that very few options are available for Cl<sup>-</sup>-intercalation materials, in a separate direction toward mitigating the issue of anion storage, a new cell architecture, referred to as cation intercalation desalination (CID) to reveal the underlying desalination mechanism, has been recently proposed by employing Na<sup>+</sup>-intercalation materials for both electrodes with the electrodes separated by an AEM (Smith and Dmello, 2016). The typical cell configuration of CID is displayed in Fig. 2g. from which we can see the principle of desalination. The CID system operates similar to rocking chair batteries, as shown by the movement of ions during alternating charging and discharging steps: during charging, Na<sup>+</sup> is removed from the negative compartment solution by the intercalating electrode while Clmigrates through the membrane leaving the negative compartment solution, resulting in a desalinated stream. The positive compartment accepted Na<sup>+</sup> from the de-intercalating electrode and Cl<sup>-</sup> passing through the membrane, resulting in a concentrated stream; During discharging, the movement of ions is reversed as well as the desalinated and concentrated effluent tanks. In contrast to cells of flow-by CDI, flow-through CDI, MCDI, i-CDI, HCDI and desalination battery requiring a regeneration step, CID cells enables a continuous production of desalinated solutions.

Smith and Dmello (2016) first introduced this novel configuration in 2016 for desalination of brackish water and seawater by using symmetric Na<sup>+</sup> intercalation electrodes (i.e., electrodes with identical chemical composition but with a different degree of intercalation) separated by either a porous separator (commonly used in sodium-ion batteries) or an AEM, and originally referred to it as Na-Ion Desalination. An ideal two-dimensional porous-electrode model was used to predict the performance of the proposed cells (Na<sub>0.44</sub>MnO<sub>2</sub>-type and NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>-type) with theoretical results indicating that AEM was able to achieve a higher degree of desalination than porous separator, and the Na<sub>0.44</sub>MnO<sub>2</sub>-based CID cell enabled a 59-64% drop in influent salinity with water-recovery levels up to 80% and 95% for 700 mM and 70 mM NaCl influent, respectively. As Na<sub>0.44</sub>MnO<sub>2</sub> and NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> are not very stable (Na<sub>0.44</sub>MnO<sub>2</sub> tends to degrade as a result of over (dis)charge while NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> tends to hydrolyze in moderate pH solutions), Smith (2017) conducted a further study in which the performance of CID cells with various membrane and flow arrangements was theoretically evaluated while the two electrodes were made from nickel hexacyanoferrate (NiHCF) Prussian Blue analogue (Na2Ni- $Fe^{(II)}(CN)_6$  as the anode and  $NaNiFe^{(III)}(CN)_6$  as the cathode) (see Fig. 18). Three CID cell designs were employed: a flow-through cell, a flow-by cell and a membrane flow-by cell. The membrane flow-by



**Fig. 18.** Schematic diagram of (a) an electrodialysis (ED) stack utilizing Na + intercalation electrodes and (b, c, d) three CID cell designs including a flow-through cell, a flow-by cell, and a membrane flow-by cell. The membrane flow-by cell is the fundamental repeat unit of ED stacks utilizing Na + intercalation electrodes. Reproduced with permission from Smith (2017). Copyright 2017 Elsevier.

cell could be scaled up to form an electrodialysis (ED) stack that utilizes Na<sup>+</sup>-intercalation electrodes rather than the gas-evolution reactions typically used in ED. Simulation results revealed that the membrane flow-by cell was superior to the other two cells (i.e., flow-through cell and flow-by cell) due to its flowability, high capacity and low polarization. Additionally, it was predicted that ED stacks using NiHCF electrodes exhibited several advantages including improved salt adsorption capacity relative to membrane flow-by cell, decreasing energy consumption per volume of diluate produced with increasing stack size, and capability of desalinating large volumes of water efficiently by continuously removing 0.4–0.5 M NaCl from 0.7 M influent within diluate streams (Smith, 2017).

Following from these two studies, the CID concept was demonstrated experimentally using symmetric Na<sup>+</sup> intercalation electrodes (Kim et al., 2017d: Porada et al., 2017) and asymmetric Na<sup>+</sup> intercalation electrodes (Lee et al., 2017b). Kim et al. (2017d) assembled a flow-by CID cell using symmetric copper hexacyanoferrate (CuHCF) electrodes and investigated effects of stack size (from single-stacked cell to triple-stacked cell) on the desalination performance of brackish NaCl solution. Experimental results were consistent with the previous predictions by Smith (2017) that stacking additional AEMs and CEMs between Na<sup>+</sup> intercalation electrodes could increase salt adsorption capacity and reduce energy consumption per volume of diluate produced. In spite of the benefits of increasing stack size, it should be pointed out that a trade-off is required between desalination performance and the need to minimize the number of IEMs due to their high cost. Porada et al. (2017) constructed a flow-behind CID cell using symmetric NiHCF electrodes and successfully demonstrated its continuous desalination of brackish NaCl/KCl solutions. Moreover, a threefold preferential adsorption of K<sup>+</sup> over Na<sup>+</sup> was observed in aqueous NaCl/KCl mixtures, which indicates the potential of NiHCF electrodes for selective ion separation from mixed ionic solutions. Lee et al. (2017b) developed a batch-mode CID cell using asymmetric Na<sup>+</sup> intercalation electrodes (NaNiHCF as the anode and NaFeHCF as the cathode) and evaluated its feasibility of treating actual seawater with experimental results showing that this system had a

high desalination capacity  $(59.9 \text{ mg g}^{-1})$  with efficient energy consumption and good stability.

Considering the high cost, imperfect permselectivity and finite lifespan of IEMs, seeking for an alternative to IEMs in CID cells is of significance. Most recently, Liu and Smith (2018) used a twodimensional porous-electrode model to study the cycling behavior of CID cell that uses porous diaphragms rather than AEM to limit salt diffusion between the two NiHCF electrodes. Though losses in charge efficiency were incurred as a result of the diaphragm's lack of selectivity toward anions, simulation results suggested that a similar desalination can be achieved in the diaphragm-based cell relative to an AEM-based cell if high enough current is applied.

Future development of CID device will benefit from on-going research in sodium-ion batteries. The materials that have been reported to exhibit reversible sodium-ion Faradaic insertion/ release in sodium-ion batteries within the decomposition voltage of water could probably be applied in CID and these materials have been summarized in Fig. 17. Meanwhile, anion intercalation desalination, representing an inverted version of CID, would be a research hotspot if Cl<sup>-</sup>-intercalation materials flourish. In addition, while CID holds great promise, some advancement could further improve performance, for example, by improving cell design through reduced internal resistances, using forced convection of electrolyte within intercalation electrodes, and flowing concentrate and dilute streams in opposing directions.

#### 4. Perspectives and outlook

It takes no more than two decades for the CDI community to develop into one of the most eye-catching research areas and it is expected that the coming years will see a further explosive growth of CDI towards a more mature and advanced technology. Nowadays, CDI embraces various cell architectures with either capacitive electrodes or battery electrodes, including flow-by CDI, flowthrough CDI, membrane CDI (MCDI), inverted CDI (i-CDI), flowelectrode CDI (FCDI), hybrid CDI (HCDI), desalination battery and cation intercalation desalination (CID), with each of them demonstrating unique features and functionalities and achieving remarkable advancements. One question has arisen from the fast proliferation of CDI cell architectures: which cell configuration is the most promising? From our perspective, it is hard to get a clear answer as each of the CDI cell architectures has unique advantages and disadvantages, and none should be neglected in future research work. For example, flow-by CDI stands out owing to its simple structure without the need of expensive IEMs or pumping energy requirements for flow-electrodes. MCDI presents higher charge efficiency than flow-by CDI at the cost of significantly more expensive cell components. Flow-through CDI allows for more compact cells and improved desalination rates but suffers from greater feed pressures than flow-by CDI for the same throughput. i-CDI features excellent operation longevity but lacks substantial salt removal capacity. FCDI exhibits continuous deionization and a high desalting efficiency but suffers from a low electronic conductivity in the flow-electrodes and additional energy cost for electrode transport. CDI cells with battery electrodes (HCDI, desalination battery and CID) regularly achieve salt adsorption capacity far exceeding that of CDI cells with capacitive electrodes. However, battery electrodes exhibit a slower salt removal and incur a higher capital cost relative to capacitive electrodes (Suss and Presser, 2018).

Flow-by CDI and MCDI are the two most widely studied cell architectures in the CDI field. A remarkable number of innovations have been realized with key aspects focusing on materials, application, operational mode, cell design, Faradaic reactions and theoretical models. Even so, the research on flow-by CDI and MCDI necessitates ongoing efforts and there are several important issues requiring a great focus in the near future: 1) Identifying the most appropriate pore size distribution of carbon-based electrodes for ion adsorption will remain the subject of further studies. While large specific surface area is a prerequisite for efficient ion adsorption, some materials with inherent high surface area vield a poor ion removal performance owing to the lack of macropores allowing for fast ion transport; 2) Recovery of the energy released during discharge is essential if (M)CDI is to become a competitive water treatment technology. As a consequence, the energy consumption with energy recovery is most likely to be a more appropriate performance metric than the energy consumption without energy recovery in future research; 3) Many works in the literature show only the first or a few initial cycles, and in some cases, even used materials with known low stability in water. Therefore, it is of importance to study the long-term desalination performance and report the cyclic stability; 4) Field tests utilizing pilot-scale or largescale (M)CDI facilities have not been adequately addressed. Such studies will provide valuable information about scalability, system cost, salinity limits, and electrode/membrane's behavior after long periods of operation, etc. Meanwhile, additional pre and post processing may need to be explored.

Desalination performance and performance stability are largely determined by the electrode material. With the emergence of HCDI, desalination battery and CID cells, the era exclusive to carbon materials for CDI electrode has ended. The exploration of battery electrodes as desalination electrodes has just begun with a great promise in desalination of high-salinity streams. To develop new cation- or anion-storage Faradaic electrode materials, it is convenient to take inspiration from the highly developed energy storage field such as ion batteries. Over the past decades, the energy storage field has developed hundreds of potential candidate materials, a deep well to explore for desalination. Many of the strategies proposed to improve the function of intercalation electrodes might be also applicable to desalination systems. It should be noted that it is also possible to have not just an electrode, but a redox-active electrolyte as the battery-electrode (Lee et al., 2018b). The electric charge can be stored in the bulk electrolyte by redox activities of the electrolyte itself. These redox electrolytes are promising for energy storage systems, particularly when they are combined with highly porous carbon electrodes. It is likely to draw inspiration from this research area to make it also applicable to the CDI field for water treatment. Other research efforts in battery electrodes derive from the problems remaining to be resolved. For example, most of battery electrodes investigated so far are only efficient for capturing a specific ion. While attractive for removal of particular ions such as key pollutants or scalants in feed waters, this selectivity limits their application in desalination of complex source waters containing multiple types of ions requiring removal, such as most brackish water and seawater. Another example is related to the stability of already proposed battery electrode materials. Like cells with capacitive electrodes, it is also important to investigate the longterm performance of cells with battery electrodes or long-term influence of co-occurrence of inorganic compounds and natural organic matter. Though researchers have claimed that these battery electrodes can be operated for hundreds of cycles without obvious performance degradation, undesired leakage of metal ions from the intercalation materials might happen during prolonged operation, potentially causing risks when used for drinking water desalination (Zhang et al., 2018a).

One exciting development in the field of CDI is the emergence of FCDI cells. By continuously replenishing the electroactive region with uncharged carbon-based materials, FCDI systems not only exhibit excellent salt adsorption capacity (>20 mg of NaCl  $g^{-1}$ )

enabling treatment of high-salinity water, but also allow for a continuous production of freshwater combined with a continuous regeneration of the electrodes. While cells with fixed-electrode such as flow-by CDI and MCDI have been extensively studied and their performance limits are largely known, FCDI is still in the initial developing stage and many possibilities for its future advances exist. Since polymer binders that have counter-productive effects on ion adsorption are not needed in the preparation of flow-electrodes, FCDI is leading to a revolutionary change in the selection of carbon materials and their synthesis. One major current challenge faced by FCDI is the inefficient charge transfer between the current collectors and flow electrodes and much work remains towards addressing this issue.

In summary, CDI is a promising water treatment technology and an exciting research field despite its related challenges. With a continuing search for solutions to these challenges and a continuing springing up of novel unexplored cell architectures, CDI may be considered as a key to solving the worldwide water shortage and water pollution in the future.

#### 5. Conclusions

Sharing many similarities with supercapacitor battery technologies in the energy storage field, CDI is an electrochemical water treatment process that operates by adsorbing ions in the electric double layers of capacitive electrodes via electrostatic interaction or in the crystal structures of battery electrodes via reversible Faradaic intercalation. The CDI field has grown exponentially over the past decade and is attracting increasing attention. Herein, a comprehensive overview of the recent advances in various cell architectures of CDI has been presented, including flow-by CDI, flow-through CDI, MCDI, i-CDI, FCDI, HCDI, desalination battery and CID, particularly the flow-by CDI and MCDI with their key research activities subdivided into materials, application, operational mode, cell design, Faradaic reactions and theoretical models. Current challenges associated with the development of various CDI cell architectures are discussed, and future research and prospects for CDI are also suggested. This review should be of great value in promoting the development of CDI technologies which may ultimately provide a sustainable, energy-saving and cost-competitive means for water treatment.

#### **Conflicts of interest**

There are no conflicts of interest to declare.

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