Faradaic reactions in capacitive deionization (CDI) - problems and possibilities: A review

Changyong Zhang\textsuperscript{a}, Di He\textsuperscript{b,c}, Jinxing Ma\textsuperscript{a}, Wangwang Tang\textsuperscript{d,c}, T. David Waite\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} School of Civil and Environmental Engineering, University of New South Wales, Sydney, NSW 2052, Australia
\textsuperscript{b} Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, China
\textsuperscript{c} Guangzhou Key Laboratory of Environmental Catalysis and Pollution Control, School of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou 510006, China
\textsuperscript{d} College of Environmental Science and Engineering, Hunan University, Changsha 410082, China
\textsuperscript{e} Key Laboratory of Environmental Biology and Pollution Control, Ministry of Education, Hunan University, Changsha 410082, China

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Capacitive deionization (CDI) is considered to be one of the most promising technologies for the desalination of brackish water with low to medium salinity. In practical applications, Faradaic redox reactions occurring in CDI may have both negative and positive effects on CDI performance. In this review, we present an overview of the types and mechanisms of Faradaic reactions in CDI systems including anodic oxidation of carbon electrodes, cathodic reduction of oxygen and Faradaic ion storage and identify their apparent negative and positive effects on water desalination. A variety of strategies including development of novel electrode materials and use of alternative configurations and/or operational modes are proposed for the purpose of mitigation or elimination of the deterioration of electrodes and the formation of byproducts caused by undesired side Faradaic reactions. It is also recognized that Faradaic reactions facilitate a variety of exciting new applications including i) the incorporation of intercalation electrodes to enhance water desalination or to selectively separate certain ions through reversible Faradaic reactions and ii) the use of particular anodic oxidation and cathodic reduction reactions to realize functions such as water disinfection and contaminant removal.

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C R O S S M A R K

Contents

1. Introduction .................................................................................................................. 315
2. Types of Faradaic reactions .......................................................................................... 316
2.1. Anodic oxidation reactions ....................................................................................... 317
2.1.1. Carbon oxidation ................................................................................................. 317
2.1.2. Chloride and water oxidation .............................................................................. 318
2.2. Cathodic reduction reactions ..................................................................................... 318
2.2.1. Dissolved oxygen reduction ............................................................................... 318
2.2.2. Carbon reduction ............................................................................................... 318
2.3. Faradaic ion storage ................................................................................................. 319
3. Negative effects of Faradaic reactions .......................................................................... 320
3.1. Desalination performance decline ........................................................................... 320
3.2. Water quality fluctuations ....................................................................................... 320
3.3. Energy loss ............................................................................................................ 321
4. Strategies to reduce/eliminate Faradaic side effects .................................................... 321

* Corresponding author.
E-mail addresses: changyong.zhang@unsw.edu.au (C. Zhang), hedy1997@gmail.com (D. He), jinxing.ma@unsw.edu.au (J. Ma), tangwangwang89@gmail.com (W. Tang), d.waite@unsw.edu.au (T.D. Waite).
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1. Introduction

With ongoing population growth and continuing industry development, the demand for freshwater has become one of the most critical global challenges of the 21st century (Elieme and Phillip, 2011; Porada et al., 2013b; Shannon et al., 2008). The United Nations Educational, Scientific and Cultural Organization (UNESCO) estimates that nearly one third of the world’s population is now living in water-stressed regions with this number expected to double by the year 2025 (UNESCO, 2009). To satisfy this demand, various water desalination technologies have been developed to produce freshwater from seawater and brackish water given that nearly 98% of the total water available falls into these categories (where “brackish water” is classified as water containing salt concentrations in the range of 1000–10,000 mg/L) (Elieme and Phillip, 2011; Georgopoulou et al., 2001; Humplik et al., 2011). Of the various water desalination technologies available (e.g. reverse osmosis and electrodialysis), capacitive deionization (CDI) is considered to be one of the most promising alternatives for desalination of waters with low to medium salinity (Porada et al., 2013b; Subramani and Jacangelo, 2015; Suss et al., 2015). The study of CDI dates back to the late 1960s and early 1970s (Caudle, 1966; Johnson and Newman, 1971; Murphy and Caudle, 1967), followed by a gap in the development of this technology between the late 1970s and mid 2000s (Porada et al., 2013b). Over the last twenty years however, breakthroughs in electrode materials and preparation (Huang et al., 2017; Liu et al., 2015), cell configurations (Gao et al., 2015b; Jeon et al., 2013; Lee et al., 2006, 2014; Suss et al., 2012), operational modes (Garcia-Quismondo et al., 2016; Zhao et al., 2012), and process modelling (Dykstra et al., 2016; Porada et al., 2013a; Tang et al., 2016) have generated renewed interest in CDI technology from both water treatment and energy recovery perspectives. As evidence of this renewed interest, the number of papers published in the CDI field has increased enormously since 2000 (Fig. 1).

In a typical CDI cell (Fig. 2), when applying a voltage difference across the two electrodes, cations are attracted to the cathode and anions to the anode, resulting in the salt ions being removed from solution. Following ion electrosorption, the electrodes can be regenerated by short-circulating the anode and cathode or executing polarity reversal, with the trapped ions released back into the brine stream (Huang et al., 2013; Suss et al., 2015; Zhao et al., 2013). There are two main mechanisms for ion storage during CDI desalination processes, i.e., non-Faradaic ion storage and Faradaic ion storage (Biesheuvel et al., 2017; Su and Hatton, 2017) with non-Faradaic capacitive ion storage the most important electrochemical process for salt removal. This process is based on the formation of an electrical double layer (EDL) at the carbon electrode where, upon applying a potential difference, ions are captured electrostatically and stored capacitively in the diffuse layer formed inside the carbon electrode intraparticle pores (Porada et al., 2013b). In order to enhance the non-Faradaic capacitive ion storage, considerable efforts have been invested in fabricating electrode materials with high adsorption capacity and sustainable use. These properties are usually associated with materials that possess high surface area, appropriate pore distribution, excellent electrical conductivity and good chemical stability (Liu et al., 2015).

Faradaic processes, although assumed by early investigators to facilitate ion removal from water (Johnson et al., 1970; Porada et al., 2013b), have not been extensively examined until recently. Whilst non-Faradaic processes are the most common phenomenon in CDI, it is now recognized that Faradaic reactions (Fig. 3) may have both negative and positive effects on CDI performance. Various types of Faradaic reactions exist in CDI systems, some of which need to be considered seriously as they may lead to (i) a decrease in electrode performance, energy efficiency and/or electrode lifespan and/or (ii) the formation of chemical by-products and/or pH fluctuations of the product water (Cohen et al., 2013, 2015; He et al., 2016; Lee et al., 2014) while others can be employed to improve desalination performance through pseudocapacitive/intercalation effects and formation of charged species. In this study, three types of Faradaic reactions are categorized as described below.

Type I are oxidation reactions that occur at the anode including carbon electrode oxidation, chloride oxidation, water oxidation and other particular contaminant oxidation reactions such as oxidation of inorganic ions and organic matters. Of these reactions, the carbon oxidation reactions have attracted the most attention given the deleterious effects that may accrue such as pore structure impairment and mass loss with subsequent decrease in carbon electrode longevity and deterioration of CDI performance (Cohen et al., 2013; Wouters et al., 2013).
Type II are reduction reactions that take place at the cathode with oxygen reduction being the most common. While it has been reported that the oxygen reduction reaction leads to the asymmetric distribution of potential of the anode and cathode with subsequent acceleration of the anodic carbon oxidation reactions (He et al., 2016), the in-situ generation of by-products such as H$_2$O$_2$ as a result of oxygen reduction might be constructively used for water disinfection (possibly via combination with UV irradiation) and/or degradation of organic contaminants provided that H$_2$O$_2$ can be effectively activated to produce more powerful oxidants. In addition, cathodic reduction reactions may contribute to the removal of heavy metals from water as a result of the possible deposition of the metals at the electrode.

Type III are Faradaic ion storage processes in which pseudocapacitive/intercalation effects are used to store ions through reversible redox reactions instead of electrostatic storage in the EDLs at the electrode/electrolyte interfaces (Chen et al., 2017a; Lee et al., 2014; Smith, 2017; Su and Hatton, 2017). Due to the superior ion electrosorption capacity of intercalation electrodes compared to traditional carbon electrodes, Faradaic ion storage processes have received considerable attention recently (Lee et al., 2014). Some of the most commonly investigated intercalation electrode materials are sodium transition metal oxides (NaTMO, TM = Mn, Ti, Fe, Ni, Co, etc., see Fig. 3b), sodium iron pyrophosphate, prussian blue analogues, for the capture of cations and conductive polymers (polypyrrole or polyaniline, see Fig. 3c), Ag/ACl, BiOCl, for the bonding of anions (Han et al., 2015; Palomares et al., 2012; Porada et al., 2017; Su et al., 2016).

In the current review, we provide a comprehensive description of the possible Faradaic reactions that could occur in CDI desalination processes. We also provide insight into both the positive and negative effects of these reactions. Guidelines and strategies that may be used to reduce or eliminate the negative side effects of Faradaic reactions are presented and approaches to best utilizing Faradaic reactions in a positive manner are described.

2. Types of Faradaic reactions

As introduced above, three major types of Faradaic reactions are addressed in this review article, namely (i) anodic reactions
associated with oxidation of the carbon electrode, chloride and water, (iii) cathodic reactions, particularly those involving oxygen reduction, and (iii) Faradaic ion storage occurring on particular redox-active electrodes.

2.1. Anodic oxidation reactions

2.1.1. Carbon oxidation

Of all the anodic Faradaic reactions in CDI systems, those involving carbon electrode oxidation are of most importance given their potential for negative impact on the performance and longevity of the system. The standard electrode potential for carbon oxidation is 0.21 V (vs. SHE) (Maass et al., 2008; Oh et al., 2008), which is likely to be within the CDI potential window when the CDI cell is operated at 1.2 V or higher. As such, during the CDI desalination process, the carbon anode might not only electrochemically store anions but may also sacrificially take part in the oxidation process with the carbon electrode initially incorporating oxygen containing groups and, potentially, eventually being converted, at least in part, into CO₂, which leads to carbon mass loss and deterioration in CDI performance. These oxidation processes may be a consequence of both direct oxidation when the anode is polarized according to Eqs (1)–(3) (Ayranci and Conway, 2001; Bayram and Ayranci, 2011; Lee et al., 2010; Maass et al., 2008; Oh et al., 2008) and indirect oxidation as a result of the anodic generation of oxidants such as chlorine and hydroxyl radicals.

\[
\begin{align*}
C + H_2O &\rightarrow C + O + 2H^+ + 2e^- \\
C + H_2O &\rightarrow C - OH + H^+ + e^- \\
C + 2H_2O &\rightarrow CO_2 + 4H^+ + 4e^- \quad E^0 = 0.21 \text{ V/SHE}
\end{align*}
\]

Strategies to evaluate the oxidation of the CDI electrodes are based on monitoring the changes in the functional groups of electrodes using methods such as X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) mapping, Fourier transform infrared spectroscopy (FTIR), acid-base titration and cyclic voltammetry (Bouhadana et al., 2011b; Chen et al., 2013; Cohen et al., 2013, 2015). The changes in the XPS oxygen (O 1s) and carbon (C 1s) intensity of the O 1s spectrum increased while the C 1s intensity decreased in the carbon anode after long-term operation, indicating that the anode acquired more oxygen containing groups during the desalination process (Cohen et al., 2013). In a similar work utilizing XPS analysis, it was found that various new oxygen-containing species were formed on the carbon electrode surface after prolonged operation although the types of these oxygen species were not fully identified (Bouhadana et al., 2011b). Cohen et al. (2015) also reported that the oxygen composition in the anode increased from 3.77 to 8.52 wt % following long-term CDI operation based on SEM-EDX results. By performing cyclic voltammetry measurements, Haro et al. (2011) revealed that the intensity of the cathodic/anodic peaks assigned to quinone/hydroquinone groups on the carbon anode increased following several cycles of CDI operation, confirming the gradual oxidation of the carbon to oxygen-containing groups. In addition, thermal analysis of these anodes suggest that the appearance of high temperature desorption bands, generally identified as CO-evolving groups, could be attributed to the incorporation of carbonyl-type groups on the carbon electrodes. These observations agree with the acid-base titration results reported by Chen et al. (2013) who found that the amount of COOH groups present in a carbon electrode increased from 0.027 to 0.391 mmol g⁻¹ after use.

Increase in resistivity and decrease in surface area and pore volume during the prolonged charging-discharging cycles have also been associated with the anodic oxidation of carbon electrodes (Cohen et al., 2015; Duan et al., 2015a; Gao et al., 2014; Haro et al., 2011; Omosebi et al., 2014). Recent results also demonstrated that oxidation of the carbon anode induced changes in pore structure with a decrease in the volume of the micropores (Bayram and Ayranci, 2011; Chen et al., 2013), the parameter recognized to contribute most strongly to ion electrosorption capacity (Porada...
et al., 2013a). As such, the prolonged anodic oxidation of carbon electrodes can be expected to lead to the deterioration of electrode structural properties with resultant desalination performance decline (Gao et al., 2014; Omosebi et al., 2014). Therefore, approaches to the reduction and/or the elimination of this Faradaic side reaction are critically required.

### 2.1.2. Chloride and water oxidation

Anodic oxidation of Cl⁻ and water may occur during the CDI electrochemical treatment of brackish waters provided anodic potentials are sufficiently positive to drive these redox reactions. The mechanisms involving the anodic oxidation of Cl⁻ are as follows: (i) the direct oxidation of Cl⁻ at the anode yields free chlorine (i.e. Cl₂) (Eq (4)), (ii) Cl₂ is rapidly hydrolyzed and disproportionates to form hypochlorous acid (HClO) (Eq (5)) and (iii) HClO and its deprotonated form ClO⁻ (Eq (6)) can be further oxidized to chlorate (ClO₃⁻) anodically (Eq (7)). Additionally, the direct oxidation of Cl⁻ to ClO₃⁻ may occur at the anode (Eq (8)) (Comminelis and Nerini, 1995; Jung et al., 2010; Martínez-Huitle and Brillas, 2009; Martínez-Huitle et al., 2015; Szpyrkowicz et al., 1994):

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \quad E^0 = 1.36 \text{ V/SHE} \tag{4}
\]

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{H}^+ + \text{Cl}^- \tag{5}
\]

\[
\text{HClO} \rightarrow \text{H}^+ + \text{ClO}^- \tag{6}
\]

\[
6\text{HClO} + 3\text{H}_2\text{O} \rightarrow 2\text{ClO}_3^- + 4\text{Cl}^- + 12\text{H}^+ + 6e^- \quad E^0 = 0.46 \text{ V/SHE} \tag{7}
\]

\[
\text{Cl}^- + 3\text{H}_2\text{O} \rightarrow \text{ClO}_3^- + 6\text{H}^+ + 6e^- \quad E^0 = 1.45 \text{ V/SHE} \tag{8}
\]

The formation of ClO₃⁻ during CDI operation has been confirmed by Lado et al. (2013) and Wouters et al. (2013) who showed that a minimal amount of ClO₃⁻ accumulated during the first 5 min whilst rapid removal of Cl⁻ occurred over this same time period. With Cl⁻ concentration approaching steady state following 10 min of charging, the production rate of ClO₃⁻ increased significantly. It was also found that the more Cl⁻ that was removed from solution, the more extensive was the generation of ClO₃⁻ in the CDI system (Wouters et al., 2013). This result suggests that Cl⁻ associated with the anode surface rather than free Cl⁻ in solution was the main contributor to the generation of ClO₃⁻. It should be noted that while a (relatively low) cathode potential of −1.74 V (vs. SHE) was reported in the above work, neither the anode potential nor charging voltage were provided. As such, quantification of ClO₃⁻ generated under more typical CDI operating conditions with well-defined anodic potential is required to properly interpret these results.

As noted earlier, the anodic oxidation of water (Eqs (9) and (10)) may also occur (Barrera-Díaz et al., 2014; Martínez-Huitle et al., 2015; Moreira et al., 2017; Sires et al., 2014):

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \quad E^0 = 1.23 \text{ V/SHE} \tag{9}
\]

\[
\text{H}_2\text{O} \rightarrow \text{HO}^- + \text{H}^+ + e^- \quad E^0 = 2.80 \text{ V/SHE} \tag{10}
\]

Although the oxygen evolution reaction (Eq (9)) exhibits a relatively lower standard redox potential than that of the chloride oxidation reaction (Eq (4)), the oxidation of Cl⁻ is likely to occur preferentially in the CDI system in view of its lower overpotential and the abundance of Cl⁻ in the vicinity of the anode during the electrosorption process (Abdel-Aal et al., 1993; Balaji et al., 2009; Bennett, 1980; Hlushkou et al., 2016; Knust et al., 2013).

To limit the extent of current leakage due to the occurrence of water electrolysis, the CDI process is typically operated at charging voltages below the limit of 1.23 V (Porada et al., 2013b). It is critical however that the anode potential be monitored over the duration of CDI operation since it is likely that (i) an asymmetric distribution of potentials of the electrodes will occur with a positive shift in potential of the anode, and (ii) significant pH fluctuations in the vicinity of the anode will occur. An anodic potential sufficient to induce oxidation of Cl⁻ to Cl₂ may be used if there is a specific desire to generate Cl₂ for either disinfection or ammonia oxidation purposes though there will obviously be a risk of current leakage due to water oxidation.

### 2.2. Cathodic reduction reactions

#### 2.2.1. Dissolved oxygen reduction

Dissolved oxygen (DO) is ubiquitous in feed waters to CDI units. As a result, Faradaic oxygen reduction reactions occur at the cathode with the possible oxygen reduction reactions shown in Eqs (12)–(14). Dissolved oxygen can be reduced either via two-electron transfer to hydrogen peroxide (H₂O₂) (Eq (12)) with E₀ = 0.69 V/SHE or four-electron reduction to water via Eq (14) with E₀ = 1.23 V/SHE (Shapira et al., 2016). In view of the evidence for the presence of H₂O₂ in CDI systems (He et al., 2016), the cathodic reduction of oxygen most likely occurs via the two-electron transfer pathway according to Eq (12).

\[
\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2 \quad E^0 = 0.69 \text{ V/SHE} \tag{12}
\]

\[
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O} \quad E^0 = 1.78 \text{ V/SHE} \tag{13}
\]

\[
\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad E^0 = 1.23 \text{ V/SHE} \tag{14}
\]

It has been reported that the CDI cathode potential is typically in the range −0.3 to −0.6 V (vs SHE), suggesting that cathodic oxygen reduction is inevitable. Recent batch-mode CDI studies have revealed that decrease in DO concentration is accompanied by formation of H₂O₂ (He et al., 2016). The reduction of DO concentration follows pseudo-first-order kinetics, i.e.,

\[
\frac{d[\text{O}_2]}{dt} = k[\text{O}_2] \tag{15}
\]

where k represents the pseudo-first-order rate constant for DO decrease. As reported by He et al. (2016), the k values increased from 5.4 × 10⁻³ to 2.7 × 10⁻² s⁻¹ with increase in charging voltage from 0.5 to 1.5 V. The steady-state concentration of H₂O₂ varied significantly with the charging voltage with H₂O₂ concentration reaching as high as 60 μM when the charging voltage was 1.2 V, as shown in Fig. 4.

Kim et al. (2016b) also reported the cathodic generation of H₂O₂ on operation of a CDI unit in single-pass mode. It was found that approximately 0.1 mg of H₂O₂ was produced over 50 operation cycles at a charging voltage of 1.2 V. Electrochemical analysis confirmed that cathodic oxygen reduction was thermodynamically favorable even at very low charging voltages (e.g., 0.5 V).

#### 2.2.2. Carbon reduction

Carbon electrodes not only undergo anodic oxidation but also experience cathodic reduction or hydrogenation (Eq (16)) resulting in the introduction of additional “C–H” groups to the carbon electrodes (Soffer and Folman, 1972). Although several research groups have mentioned the possibility of occurrence of carbon
reduction in their CDI systems (Chen et al., 2013; Lado et al., 2014), there has been no conclusive evidence presented to date to confirm the occurrence of this reaction (nor its standard potential).

\[ C + H_2O + e^- \rightarrow C - H + OH^- \] (16)

The range of redox potentials over which the main Faradaic reactions occur on the CDI anodes and cathodes and typical electrode working potentials as a function of cell voltage are shown in Fig. 5 (Holubowitch et al., 2017). The potential map provides a very useful practical guide for optimization of cell voltage such that side Faradaic reactions are minimized.

2.3. Faradaic ion storage

Faradaic ion storage processes involve the application of intercalation electrodes (mainly transition metal containing material or conductive polymer) for ion harvesting from saline waters. The ion storage mechanisms involve the trapping of ions into the crystallographic sites of the intercalation materials via redox reactions with this process fundamentally different from the EDL charging process occurring within conventional carbon electrodes. Due to the exemplary salt electro-adsorption capacity and potential ion selectivity of these electrodes, Faradaic ion storage processes are attracting increasing attention.

Interest in Faradaic desalination has been inspired by sodium and lithium ion battery systems. Transition metal-containing materials have been most commonly used for cathode construction while preparation with sodium manganese oxide \( (Na_{0.44}MnO_2, Na_2Mn_5O_10) \), lithium manganese oxide \( (Li_3MnO_4) \), sodium iron pyrophosphate \( (Na_2FeP_2O_7) \), sodium nickel hexacyanoferrate \( (NaNiHCF) \) and sodium iron hexacyanoferrate \( (NaFeHCF) \) are of most interest in view of their capacity to trap alkali metal ions such as \( Na^+ \) and \( Li^+ \) but lower preference for ions such as \( Mg^{2+} \) and \( Ca^{2+} \) (Chen et al., 2017a, 2017b, Lee et al., 2014, 2017; Missoni et al., 2016; Porada et al., 2017). Examples of reactions occurring at these cathodes are provided in Eqs (20) and (21):

\[ Na_{0.44-x}MnO_2 + xNa^+ + xe^- \rightarrow Na_{0.44}MnO_2 \] (20)

\[ xLi + Li_{1-x}Mn_{1-x}^{III}Mn_{x}^{IV}O_2 + xe^- \rightarrow Li^{x}Mn^{IV}Mn^{III}O_4 \] (21)

There appears to be much less choice for the anode. Silver, conductive polymers or BiOCl have been reported to be effective for the capture of chloride ions, the most common anions in the saline water (Chen et al., 2017a, 2017b; Missoni et al., 2016). Examples of reactions taking place at the anodes are shown in Eqs (22)–(24):

\[ Ag + Cl^- \rightarrow AgCl + e^- \] (22)

\[ xCl^- + xPP_{0} \rightarrow x\left[ PP^+Cl^- \right] + xe^- \] (23)

\[ Bi + Bi_2O_3 + 3Cl^- \rightarrow 3BiOCl + 3e^- \] (24)
Detailed discussion of the applications and desalination performances of Faradaic electrodes is presented in Section 5.1.

3. Negative effects of Faradaic reactions

As mentioned earlier, the aging of carbon electrodes, due particularly to anodic oxidation of electrode materials over long-term CDI operation, results in numerous side effects such as desalination performance decline, water quality fluctuations and undesirable energy consumption.

3.1. Desalination performance decline

CDI cells are usually (depending on the design) initially symmetrical with the potentials of the anodes and cathodes identical, assuming they possess the same surface area and pore distribution (Bouhadana et al., 2011a; Cohen et al., 2015; Cohen et al., 2011). After a number of cycles of charging and discharging operation, the distribution of potential between the anodes and cathodes ceases to be symmetrical due to the occurrence of Faradaic side reactions (e.g. the reduction of oxygen that inevitably occurs at the cathode) with a positive shift in potential of the anodes. Consequently, the anode potential may exceed its potential limit of stability, leading to the occurrence of anodic carbon electrode oxidation. In turn, changes in the structure of the electrodes due to anodic oxidation may further drive the CDI cell away from symmetric behavior with the occurrence of Cl⁻ and water oxidation (see Section 2 for further details), finally resulting in decline in the charge efficiency and the desalination performance.

There have been several studies showing the decline in desalination capacity and charge efficiency during prolonged CDI operation (Bouhadana et al., 2011a; Cohen et al., 2013; Gao et al., 2015b; Lu et al., 2017). Gao et al. (2015b) conducted a detailed investigation with CDI cells equipped with 16 pairs of pristine carbon xerogel electrodes at charging/discharging voltages of 1.2/0 and 0.8/0 V. As shown in Fig. 6a and b, both the electrosorption capacity and charge efficiency declined significantly with an increase in the cycle number during the prolonged cycling tests. A more rapid decline in the desalination performance was observed on increase in the charging voltage from 0.8 to 1.2 V. Similarly, Lu et al. (2017) observed severe CDI performance degradation, with the salt electrosorption capacity declining from 7.3 to 0.5 mg g⁻¹ after 70 cycles in symmetric 1.2/0 V operation. Another recent study also reported that the charge efficiency dropped sharply (from 92% to 69.5%) and was accompanied by a dramatic increase in cell voltage (from 0.6 to 4.8 V) due to the occurrence of inevitable Faradaic reactions. Despite these changes, the rate of ion adsorption increased significantly (by around 7 times) (Liang et al., 2017). An indicator of CDI performance decline after prolonged charge-discharge cycles relates to the occurrence of a so-called “inversion effect”, which was reflected by the occurrence of ion desorption (i.e. a rise in effluent conductivity) during charging. In turn, ions are adsorbed and trapped in the electrodes (i.e. effluent conductivity decreases) on cell discharge (Bouhadana et al., 2011a).

3.2. Water quality fluctuations

As mentioned above, the occurrence of Faradaic reactions at the CDI electrodes may lead to pH fluctuations and the formation of chemical byproducts, leading to severe fluctuations in the effluent water quality. He et al. (2016) reported that the effluent pH varied significantly with different charging voltages in a batch-mode CDI cell. Upon applying a charging voltage of 0.9 V, the pH rapidly climbed to ~10 and then reached steady state while the effluent pH increased slightly and then decreased rapidly at charging voltages higher than 1.2 V, which was in agreement with other studies (Lado et al., 2014; Lee et al., 2010). Cohen et al. (2013) also reported that over long-term CDI operation (13 days), the pH shifted to more acidic conditions with pH fluctuations particularly severe during charging at 0.9 V, while the pH fluctuations were insignificant and within the pH range of 6–7 when the CDI cell was charged at a lower voltage of 0.7 V. Interestingly, the pH in the vicinity of the electrodes was significantly different to that in the bulk solution. A highly inhomogeneous pH environment appeared during the water desalination processes, with the near-anode and near-cathode pH reaching 2.4 and 10.3 under a typical operation voltage of 1.2 V, respectively (Holubowitch et al., 2017). Litmus-paper was used in an earlier study to roughly measure the near-electrode pH values and revealed that the pH close to the anode can decrease to as low as 2–3 while the pH at cathode can climb higher than 10 (Choi, 2014).

According to Eqs (12) and (14), the oxygen reduction reactions at the cathode consume H⁺ with these reactions the dominant Faradaic processes occurring when the voltage is relatively low (e.g. < 1.0 V), resulting in pH increase (Lee et al., 2010). With an increase in the charging voltage, carbon electrode oxidation reactions start to occur (Eq (3)) with the release of H⁺ into solution. As the charging voltage further increases, Cl⁻ and water oxidation could take place at the anode (Eqs (4)–(8)). Most of these oxidation reactions are capable of generating H⁺, resulting in a decrease in the pH of the treated stream. Other interpretations of observed pH variations on operation of CDI systems could be attributed to the difference in ion mobility of H⁺, OH⁻ and other ions and/or the non-Faradaic preferable electrosorption of these ions (Andres and Yoshihara, 2016; Han et al., 2013; Porada et al., 2013b). Interestingly, Dykstra et al. (2017) presented a model enabling the prediction of pH changes in the MCDI cell. They found that although the different mobilities of various ions contributed to the pH fluctuation of the effluent, Faradaic reactions played a more important role in relation to pH changes during CDI operation. Bouhadana et al. (2011b) reported that the pH fluctuation was dramatically reduced when replacing dissolved air with nitrogen (by bubbling nitrogen gas into the solution), suggesting that the pH fluctuation depends strongly on Faradaic reactions involving oxygen at the electrodes.

While it has been reported that change of pH exerted an insignificant influence on salt removal during CDI operation (Porada et al., 2012a), significant effluent pH fluctuations remain problematic. For example, when cations such as Ca²⁺ and Mg²⁺ are present in the feed water, scale formation on the surface of the cathodes is likely to be a problem, particularly at higher pHs where carbonate minerals containing these cations readily form (Choi and Kang, 2016). It is also worthwhile mentioning that the stability of some of the redox-active electrodes (such as those made from transition metal oxide/carbon composites) is likely to depend strongly on pH. A rapid decrease of pH in the vicinity of the anodes could lead to the undesirable leakage of metal ions from the metal oxide composites, potentially posing significant health risks to consumers.

In addition to pH fluctuations, Faradaic reactions may also generate undesired byproducts during charging and discharging cycles. One example is the production of ClO₃⁻, which, as described earlier, could be generated upon the oxidation of Cl⁻ at the anode (Wouters et al., 2013). The presence of high concentrations of ClO₃⁻ in effluents represents serious health risks for both humans and animals (Srinivasan and Sorial, 2009) with deleterious effects including oxidative damage to erythrocytes and mutagenic activities in mammalian cells (Jung et al., 2010; Richardson et al., 2007).
Due to these toxic effects, the WHO has proposed a threshold limit for \( \text{ClO}_3^- \) in drinking waters of \(<0.7 \text{ mg L}^{-1} \) (Edition, 2011). As such, effective strategies must be implemented to prevent the generation of \( \text{ClO}_3^- \) and its derivative by-products if CDI is applied to drinking water purification.

### 3.3. Energy loss

Faradaic reactions (also referred to as ‘parasitic electrochemical charge transfer’), leakage currents and ohmic losses are the main reasons that the energy efficiency declines, possibly by 20–30%, over months of operation (Farmer et al., 1996). Recent studies of the energy loss mechanisms in CDI units under constant current (CC) operation reveal that resistive and parasitic losses, primarily due to leakage currents associated with Faradaic reactions at the electrodes, are the two major sources of energy loss (Hemmatifar et al., 2016). Results of these studies indicate that resistive energy loss was dominant under high current conditions as it increases approximately linearly with current for fixed charge transfer. On the other hand, parasitic loss dominated in low current cases as the electrode is held at higher voltages for a longer period of time. Compared to operation in CC mode, the energy loss in constant voltage (CV) mode is more significant mainly due to the higher resistive dissipation, as well as the longer charging time spent at higher oxidizing potentials (Qu et al., 2016).

### 4. Strategies to reduce/eliminate Faradaic side effects

As described previously, Faradaic reactions may cause a range of negative side effects over prolonged CDI operation including desalination performance decline, water quality fluctuations and undesirable energy consumption. A variety of strategies may be envisaged to reduce/eliminate these Faradaic side effects including optimization of the CDI configuration, modification of CDI operation mode and fabrication of novel CDI electrodes.

#### 4.1. Alternative CDI configurations

##### 4.1.1. Membrane capacitive deionization

Membrane capacitive deionization (MCDI) is a significant improvement over conventional CDI and involves the incorporation of ion-exchange membranes (IEMs) in front of the CDI electrodes thereby enabling more selective ion adsorption and desorption (Li et al., 2008). Incorporation of IEMs in CDI is also recognized to be an effective method to alleviate particular Faradaic reactions including the cathodic reduction of oxygen and anodic oxidation of carbon (Omosebi et al., 2014).

Tang et al. (2017) compared the Faradaic reactions occurring in CDI and MCDI cells equipped with carbon cloth electrodes through investigation of \( \text{H}_2\text{O}_2 \) production and DO decay. During charging, \( \text{H}_2\text{O}_2 \) was generated with a steady-state concentration of up to 60 \( \mu \text{M} \) in the CDI cell due to DO reduction at the cathode (Eq (12)) while less than 2 \( \mu \text{M} \) \( \text{H}_2\text{O}_2 \) was observed in the MCDI cell. This was consistent with the observation that DO decreased rapidly to \(<1 \text{ mg L}^{-1} \) in the CDI cell while insignificant decay of DO was observed in the MCDI cell. As reported previously, the oxygen diffusivity in Neosepta and Nafion membranes is two orders of magnitude smaller than that in water (Ogumi et al., 1984). Consequently, IEMs incorporated in CDI units act as efficient barriers to transport of DO to the cathode thereby inhibiting oxygen reduction reactions at the cathode in the MCDI cell. The elimination of cathodic oxygen reduction could contribute to the alleviation of the positive shift of potential distribution to the anode over long-term CDI operation (Bouhadana et al., 2011b; Cohen et al., 2013).

More interestingly, some researchers presented the effects of Faradaic reactions on the long-term performance of CDI and MCDI units equipped with carbon xerogel electrodes (Omosebi et al., 2014). Unlike CDI which was found to experience severe desalination performance decline in a short period of time, MCDI exhibited stable performance over the 50 h of operation. Post-testing evaluation of the used CDI anode showed a positive shift of \( E_{\text{PZC}} \) by 0.5 V after 50 h operation, while the voltage increase of the anode \( E_{\text{PZC}} \) was only 0.2 V in the MCDI cell. These results clearly demonstrate that the carbon oxidation reactions were suppressed by the incorporation of IEMs into the CDI unit (more details in Section 3.1).

#### 4.1.2. Inverted capacitive deionization

Gao et al. (2015b) proposed a new CDI configuration, termed inverted capacitive deionization (i-CDI), with the aim to diminish side effects of Faradaic reactions and achieve stable and efficient
desalination performance. The i-CDI system involves the use of an anode with net negative surface charge and a cathode with net positive surface charge. Interestingly, salt removal in this novel i-CDI system was achieved in a manner completely opposite to traditional CDI systems with cell charging leading to ion desorption from the EDLs of the electrodes while cell discharging by short-circuiting the anode and cathode led to ion adsorption (Fig. 6a and b). Most importantly, desalination performance was shown to be maintained for over 600 h; an improvement in lifetime of the system by 530% compared to that of a conventional CDI system operated under similar conditions. In a more recent work, Gao et al. (2015a) developed an amine-treated anode (with $\text{NH}_3$ groups providing positive surface charge) and acid-treated carbon cathode (with COO$^-$ groups providing negative surface charge) and achieved a desalination capacity of 5.3 mg g$^{-1}$ at charging/discharging voltages of 1.1/0 V with this performance representing a significant improvement with regard to both salt removal capacity and working voltage window compared to the first-generation of i-CDI systems. Wu et al. (2016) further fabricated an i-CDI system equipped with an activated carbon cathode modified by poly (4-vinylpyridine) and a carbon anode treated with nitric acid and achieved a remarkably high salt removal capacity of 20.6 mg g$^{-1}$.

In i-CDI systems, the oxidation of the anode is not regarded as an adverse effect as is the case in conventional CDI systems. Indeed, oxygen-containing functional groups formed during the carbon oxidation process increase the net negative surface charge thereby further expanding the available internal working voltage window for salt separation performance (Fig. 7c). As a consequence, the formation of oxide thin-layers at the anode could contribute to a significant improvement in CDI desalination stability in long-term operation, paving a new way for high performance CDI.

4.1.3. Flow-electrode capacitive deionization

Flow-electrode capacitive deionization (FCDI) is an innovative MCDI method using suspended carbon slurry that flow in the flow channels carved on the current collectors. FCDI exhibits a number of distinctive benefits for water desalination, i.e., excellent ion-adsorption capacity, continuous desalination behavior, and potentially energy and resource recovery if designed and operated appropriately. It has been reported recently that the anode pH could decrease to 1.5 while cathode pH increased to 12.5, when the FCDI was operated in a separated flow electrode mode (anode and cathode slurry flowing separately) (Nativ et al., 2017). However, when using the combined flow-electrode (the anode and cathode flow electrodes mixing outside the FCDI cell), the Faradaic reaction could be partly suppressed with the combined flow-electrode pH stabilized at around 7 and the energy consumption much lower compared to the separated flow-electrode CDI.

4.1.4. Flow-by and flow-through capacitive deionization

Flow-by and flow-through CDI (are two types of common CDI configurations (Guyes et al., 2017; Suss et al., 2012). A recent comparison of the long-term stability of these two configurations during desalination indicated that use of a flow-by configuration could enhance the CDI cell stability by up to 360% compared to the flow-through configuration with a lifetime of 18 days compared to 5 days (Cohen et al., 2015). As such, flow-by CDI is considered to be a better configuration than flow-through CDI, mainly due to the presence of a hydrodynamic diffuse boundary layer which prevents rapid transport of dissolved oxygen to the surface of the cathode. The limitation of oxygen reduction on the cathode results in the reduction of an asymmetric distribution of potentials in flow-by cells.

4.2. Operational approaches

4.2.1. Optimization of the voltage window

As reported by Lu et al. (2017), CDI underwent significant performance decline even when operated at a voltage as low as 1.2 V. To mitigate the performance decline, they tested a number of different charging and discharging voltages, and finally obtained the optimal operation voltage window to be charging at 0.8 V and discharging at $-0.4$ V. The CDI system exhibited a slightly lower desalination capacity (6.3 mg g$^{-1}$) under this voltage window compared to that of the 1.2/0 V experiment (7.3 mg g$^{-1}$). Nevertheless, it is an important finding that carbon oxidation was inhibited in this optimal voltage window with negligible performance degradation observed, even after more than 70 operation cycles.

4.2.2. Constant current operation

To reduce Faradaic reactions, one straightforward and effective

![Fig. 7. Schematic of (a) capacitive deionization, (b) inverted capacitive deionization, (c) the working voltage window for the i-CDI. Adapted with permission from Gao et al. (2015b). Copyright 2015 Royal Society of Chemistry.](image)
method is to apply a lower charging voltage to the CDI cells. Indeed, there always exists a conflict between mitigation of anodic oxidation of carbon electrodes and enhancement of desalination performance. Based on the Gouy-Chapman-Stern model, higher charging voltage applied to the CDI cell results in improvement of ion electrosorption capacity while the higher voltage could lead to increased anodic oxidation of the carbon electrodes over prolonged CDI operation (Zhao et al., 2009). As such, CC mode is more favorable than CV mode since electrodes are exposed to higher voltages for less time resulting in lower resistive and parasitic losses during CC compared to CV operation (Qu et al., 2016).

4.2.3. Periodic electrode polarity reversal

It has been found that the decline in CDI electrosorption capacity on aging of the carbon electrodes can be recovered to a large extent by periodically reversing the cell polarity (Cohen et al., 2015; Farmer et al., 1996). Cohen et al. (2015) have examined this possibility and found that when the CDI unit was operated periodically according to the following four steps: (i) 0.9 V, (ii) 0 V, (iii) –0.9 V, (iv) 0 V, with each step lasting for 30 min, the desalination performance showed no obvious decline even after running for 34 days while control experiments with the charging/discharging cycle of 0.9 V/0 V achieved only 5 days of stable operation. The pH fluctuations were only in the range of 5.8–7, indicating reasonable stability of the cell. Unlike the regular behavior of the conventional CDI with one electrode serving as the anode and the other as the cathode during charging, in periodic polarity reversing mode each electrode periodically serves as anode or cathode. This operation provides an identical working condition for both electrodes in long-term operation, thereby avoiding the asymmetric shifting of the $E_{fs}$ between two electrodes and thus suppressing the Faradaic reactions, especially reducing the rate and extent of the oxidation of the electrodes (Cohen et al., 2015).

Similarly, Gao et al. (2017) reported desalination performance of the CDI stack equipped with carbon xerogel electrodes by alternating polarization of ±1.2/0 V. Long-term operation suggested that this operational mode could eliminate the formation of inversion peaks thereby effectively extending the cycling stability for salt ion removal. The surface charge of both carbon electrodes gradually shifted from “positively charged” to “negatively charged” due to the inevitable and irreversible Faradaic reactions as each electrode alternately served as CDI anode during this alternating polarization process. These studies also demonstrated for the first time that the highest salt adsorption capacity was attained after 200-h of operation when the positively and negatively charged surface sites on the electrodes became nearly equal.

4.2.4. Deoxygenation cell

As demonstrated previously, the presence of dissolved oxygen results in undesirable oxygen reduction reactions at the cathode even under a low operating voltage. Use of a low-cost deoxygenation cell to remove dissolved oxygen before the water enters the CDI cell results in inhibition of the oxygen reduction reaction and suppresses its competition with the cation capacitive adsorption, thereby resulting in an enhanced salt adsorption capacity and reduced energy consumption (Holubowitch et al., 2017).

4.3. Novel CDI electrode fabrication

Recent studies have demonstrated that the impregnation of certain types of polymers could effectively suppress the Faradaic effects. Choi and Choi (2010) fabricated carbon electrodes by mixing the activated carbon powder with polyvinylidene fluoride (PVDF) binder and showed that the Faradaic current decreased significantly with increase in the PVDF content of the carbon electrodes. Further investigations suggested that the polymer binder reduced the redox activity of the functional groups (i.e., carbonyl- or quinone-type oxygen functional groups) on the carbon surface (Hsieh and Teng, 2002). In addition, a novel polymer-impregnated carbon anode involving coating a mixture of the Type I strong base anion resin N-methyl-2-pyrrolidone (NMP) and PVDF onto carbon cloth was fabricated by Gao et al. (2016). The experimental results showed that stable desalination performance and higher charge efficiency with much less significant effluent pH fluctuations were obtained using this novel anode. Meanwhile, the $E_{fs}$ of the pristine anode shifted positively by ~0.26 V whereas the polymer-coated anode showed minimal obvious $E_{fs}$ shift after prolonged operation demonstrating that the coverage of anion-exchange polymer layers could effectively mitigate the anodic oxidation of carbon electrodes.

Srimuk et al. (2016) chemically modified activated carbon (AC) electrodes with titania, which could provide additional catalytic activity for oxygen-reduction reactions at the cathode and preventing oxidation of the carbon electrode. The study revealed that titania coated AC electrodes exhibited higher desalination capacity and better long-time stability than pure AC electrodes in oxygen saturated NaCl solution. After 15 operating cycles, the AC-titania hybrid electrode presented a comparable high salt removal capacity of 8 mg g$^{-1}$ whereas CDI with the pure AC electrodes lost almost all the desalination capacity. It was shown that pure AC electrodes exhibited the oxygen reduction reaction in a two-electron transfer and produced H$_2$O$_2$ which was then used to attack the carbon electrodes, resulting in a decline in desalination performance. In contrast, AC-titania electrodes consumed the oxygen via a three-electron transfer reaction that suppressed the formation of H$_2$O$_2$ preventing the carbon electrode from being oxidized and partially reducing the deterioration of the CDI desalination performance.

5. Positive applications of Faradaic reactions

Although Faradaic reactions are generally recognized to cause serious problems including electrode deterioration and associated desalination performance decline, water quality fluctuations and undesirable energy loss, some Faradaic reactions may contribute to the enhancement of desalination performance and/or may contribute to the achievement of CDI multifunctionality (such as simultaneous desalination and disinfection/micropollutant degradation). These possibilities are discussed briefly below.

5.1. Desalination performance enhancement

5.1.1. Faradaic ion storage

Over the past few years, researchers have been focusing on optimization of traditional CDI systems equipped with static porous carbon electrodes and have achieved salt adsorption capacities approaching ~15 mg g$^{-1}$. For flow carbon electrode system, a slightly higher salt adsorption capacity of ~20 mg g$^{-1}$ is expected. Due to the low intrinsic charge storage capacitance of porous carbon electrodes, however, a CDI device based on the mechanism of non-Faradaic capacitive adsorption (ion storage in the EDLs of carbon micropores) suffers from the limitation of improvement of salt adsorption capacity. As mentioned in Section 2.3, an alternative means of enhancing ion storage is to employ innovative pseudocapacitive electrodes which extract ions through reversible Faradaic reactions that occur on intercalation of ionic species within the electrodes, with advantages particularly in the desalination of highly concentrated saline water and in the selective harvesting of particular ions. A comparison of desalination performance among electrodes based on EDL and Faradaic ion storage mechanisms is presented in Table 1.
Following the pioneering attempts at using pure Faradaic-based CDI cells in which sodium-manganese oxide (Na₂Mn₅O₁₀) was employed as the cathode for sodium capture while Ag/AgCl served as the anode for chloride capture (Pasta et al., 2012), a modified hybrid CDI cell was proposed by Lee et al. (2014). This hybrid CDI cell was comprised of a Faradaic type cathode (sodium-manganese oxide materials, Na₂Mn₅O₁₀) and a non-Faradaic type anode (porous carbon materials) and exhibited a desalination capacity of 31.2 mg g⁻¹—twice as high as that for pure carbon capacitive electrodes. In their subsequent work (Kim et al., 2016a), sodium iron pyrophosphate (NaFeP₂O₇) electrodes (which served as the Faradaic cathode) were developed with this hybrid CDI system achieving a reasonably high electrosorption capacity (30.2 mg g⁻¹). Porada et al. (2017) prepared a novel porous electrode which contained redox-active nickel hexacyanoferrate (NiHCF) nanoparticles and used them for electrochemical water desalination. When applying a current density of 2.8 A m⁻², a high electrosorption capacity (34 mg g⁻¹) was achieved, 1.5 times higher than that of the CDI with carbon electrodes (12.5 mg g⁻¹). Meanwhile, the current efficiency reached 80%–95% and energy costs of desalination were significantly reduced. Chen et al. (2017a,b) reported a similar Faradaic capacitive deionization cell based on Na₀.₄₄MnO₂ cathode and Ag/AgCl anode for chemical intercalation and deintercalation of sodium and chloride ions with this electrode system exhibiting a stable and reversible desalination capacity of 57.4 mg g⁻¹ after 100 cycles of operation with an excellent charge efficiency of 97.9%/95.6% during the charging/discharging process. More recently, another novel Faradaic capacitive-based desalination system was developed with sodium nickel hexacyanoferrate (NaNiHCF) and sodium iron HCF (NaFeHCF) as the electrodes (Lee et al., 2017). One interesting aspect of this cell is that desalination took place not only during the charging step but also the discharging step, achieving the continuous desalination brackish water with a high desalination capacity (59.9 mg g⁻¹) and efficient energy consumption (5–10 W hh mol⁻¹). Following this work, Kim et al. (2017) developed a similar CDI system using identical copper hexacyanoferrate (CuHCF) electrodes to bind sodium and chloride separated via the anion exchange membrane with this cell realizing a desalination capacity of nearly 100 mg g⁻¹. Most recently, dual-ion electrochemical desalination systems, using Na₀.₄₄MnO₂ as the sodium ion Faradaic electrode and BioCl as the chloride ion Faradaic electrode have been explored. An extremely high salt capture capacity of 68.5 mg g⁻¹ and a charge efficiency of 97.7% were achieved (Chen et al., 2017b) with these results suggesting a promising future for highly saline water desalination.

While a variety of electrodes have been fabricated for the selective intercalation of cations, only a few have been developed for the capture of anions. Missoni et al. (2016) developed an alternative LiMn₂O₄-polyacrylate electrochemical cell to selectively capture lithium chloride from seawater or other natural brine solution. Chloride ions were successfully extracted by the polyacrylate coated carbon felt anode while the lithium ions were effectively harvested in the LiMn₂O₄ cathode. Upon applying a low potential difference of 0.6–1.1 V, a competitive charge efficiency of 50% with energy consumption of 5–10 W hh mol⁻¹ was achieved with excellent reproducibility over 200 cycles.

In addition to removal of salts (cations and anions) from aqueous solution, Faradaic ion storage has also been applied to the selective separation of charged organic matter from electrolyte solutions containing strong inorganic salts as well as dilute organic pollutants. Su et al. (2016) developed a system comprised of carbon electrodes coated with redox-active material (PVF/CNT) which exhibited excellent selectivity towards organic anions (carboxylates (−COO⁻), sulfonates (−SO₃⁻), and phosphonates (−PO₃³⁻)) with a separation factor of more than 140 and 3000 times compared to inorganic anions (PF₆⁻ and ClO₄⁻) in aqueous and organic solutions, respectively. In later studies, a similar system with organometallic functionalized redox-cathode and ferrocene-modified redox-anode was used in an asymmetric electrochemical capacitive cell and demonstrated a remarkable degree of selectivity for the retention of charged micro-pollutants (such as pesticides, endocrine disruptors, and pharmaceuticals) with a current density of up to 96%. Their findings provide a promising and energy-efficient pathway for the capture/recovery of value-added products and/or the separation/isolation of dilute but highly toxic organic pollutants from aqueous or organic systems (Su et al., 2017).

Although Faradaic ion storage is a promising area and one in which there is considerable interest, several problems still remain to be solved.

(i) Most intercalation electrodes are only efficient for capture of particular ions; for example, sodium manganese oxide (NMO) can selectively take up Na⁺ while NiHCF shows affinity for K⁺. While attractive for removal of particular ions, this selectivity limits their application with regard to treatment of source waters containing multiple types of ions including Na⁺, K⁺, Ca²⁺ and Mg²⁺;

(ii) There is a lack of materials that can serve as the anion-storage electrodes in aqueous media. Although Ag/AgCl was found to be a highly efficient Cl⁻ ion capture electrode, its further application is likely to be limited by commercial constraints. More studies should be focused on the development of cost-effective, efficient and stable intercalation electrodes for anions, such as Cl⁻, F⁻, NO₃⁻, SO₄²⁻, from saline waters;

(iii) Although researchers have claimed that these Faradaic electrodes can be operated for hundreds of cycles without significant decrease in desalination performance, undesired leakage of metal ions from the intercalation materials might occur during prolonged operation, potentially causing risks when used for drinking water desalination (Bouchard et al., 2011; Dion et al., 2016).

5.1.2. Electron mediators

Another innovative application of Faradaic reactions in desalination enhancement involves the introduction of redox-active electron shuttles (such as quinones) into FCID systems where aqueous suspensions of activated carbon particles flow through a channel carved on the current collector (Ma et al., 2016). The quinone species in the flow-electrode acted as an electron mediator with redox transformation between the reduced hydroquinone (H₂Q) and oxidized benzoquinone (Q) forms of the quinone occurring at the electrode surface and electrolyte interface (Fig. 8a). The presence of the H₂Q/Q couple in the flowing carbon suspension significantly accelerated the charge transfer between the carbon particles and current collectors, thereby enhancing both the salt electrosorption and desorption processes (Fig. 8b). On applying a charging voltage of 1.2 V, the average salt removal rate increased by ~131% on adding H₂Q at a concentration of 14 mM to a 1 wt% activated carbon suspension, with a similar positive effect observed during the discharging process. This result represents a breakthrough in the development of FCID with the application of Faradaic reactions providing a highly efficient means for enhancing desalination performance.
5.2. Other Faradaic applications

5.2.1. Disinfection

As described previously, active species such as HClO, HO\(_2\)/C\(_1\) and H\(_2\)O\(_2\) can be generated through the occurrence of Faradaic reactions in a CDI cell with these species potentially of use in water disinfection. Laxman et al. (2015) evaluated the bacterial inactivation properties of a CDI cell with activated carbon cloth electrodes and observed an approximate 3-fold reduction in the number of viable bacterial colonies (from 3 \times 10^4 CFU mL\(^{-1}\) in the feed water) following CDI operation. Another group fabricated a novel electrode by impregnating cationic nanohybrids of graphene oxide grafted quaternized chitosan to activated carbon electrodes (GO-QC/AC) (Wang et al., 2015). A CDI cell equipped with this novel electrode achieved an ultrahigh inactivation rate (i.e., 99.9999% or 6 log reduction) of *Escherichia coli* during water desalination. However, a CDI unit with pristine activated carbon electrodes removed less than 82.8% of the viable bacteria present in feed waters.

Although the mode of antimicrobial action by CDI has not yet been clearly elucidated, the active oxidants (e.g. HClO and HO\(_2\)/C\(_1\)) generated during the electrochemical process could play an important role in this process (Jeong et al., 2006).

### Table 1

Comparison of the desalination performance among electrodes based on the EDL ion storage mechanism and Faradaic ion storage mechanism.

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>Operation voltage/Current density</th>
<th>Initial salt concentration (mM)</th>
<th>Electroadsorption capacity (mg g(^{-1}))</th>
<th>Charge efficiency</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDL electrode</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathode/anode:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon aerogel</td>
<td>1.2 V 8.5 2.9 n.a.</td>
<td>(Farmer et al., 1996)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathode/anode:</td>
<td>2.0 V 0.4 1.8 n.a.</td>
<td>(Li et al., 2009)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphene</td>
<td>1.2 V 3.4 84%</td>
<td>(Kim and Choi, 2010)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathode/anode:</td>
<td>1.2 V 5 69%</td>
<td>(Porada et al., 2012b)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activated carbon</td>
<td>1.5 V 50 43%</td>
<td>(Suss et al., 2012)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Carbon aerogel</td>
<td>1.2 V 8.5 14.5 50%</td>
<td>(Xu et al., 2015b)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphene sponge</td>
<td>1.2 V 8.5 18.7 55%</td>
<td>(Xu et al., 2015a)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon nanotubes@ graphene</td>
<td>1.2 V 5.1 9.2 n.a.</td>
<td>(Wang et al., 2016)</td>
<td></td>
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<tr>
<td>Faradaic electrode</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Cathode: Na(_4)Mn(_9)O(_18)</td>
<td>1.2 V 100 31.2 n.a.</td>
<td>(Lee et al., 2014)</td>
<td></td>
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<tr>
<td>Anode: activated carbon</td>
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</tr>
<tr>
<td>Cathode: Na(_2)NiFe(CN)(_6)</td>
<td>2.8 A m(^{-2}) 20 34.0 80%</td>
<td>(Porada et al., 2017)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anode: Na(_0.44)MnO(_2)</td>
<td>3.0 A m(^{-2}) 15 57.4 98%</td>
<td>(Chen et al., 2017a)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anode: AgCl</td>
<td>5.0 A m(^{-2}) 500 59.9 83%</td>
<td>(Lee et al., 2017a)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathode/anode: Na(_0.44)MnO(_2)</td>
<td>5.7 A m(^{-2}) 13 68.5 97.7%</td>
<td>(Chen et al., 2017b)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anode: BiOCl</td>
<td>5.7 A m(^{-2}) 13 68.5 97.7%</td>
<td>(Chen et al., 2017b)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathode/anode: CuHCF</td>
<td>2.8 A m(^{-2}) 50 (<del>100</del>) 80%</td>
<td>(Kim et al., 2017)</td>
<td></td>
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</table>

* Cathode/anode means that the CDI used the asymmetry electrode, with the anode and cathode to be the same material.

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**Fig. 8.** (a) The mechanism of charge transfer in the anode flow-electrode chamber when adding aqueous hydroquinone (H\(_2\)Q) and benzoquinone (Q) as the electron shuttle. (b) Temporal variation of the salt concentration in the FCDI cell using blank flow-electrodes (1 wt% dispersion of activated charcoal) or redox-active flow-electrodes containing 14 mM H\(_2\)Q (w/H\(_2\)Q). Reprinted with permission from Ma et al. (2016). Copyright 2016 American Chemical Society.
In addition, the H₂O₂ generated via cathodic oxygen reduction, if combined with UV irradiation or O₃, would also be expected to result in bacterial inactivation. Indeed, previous studies have demonstrated that low concentrations of H₂O₂ (20–150 μM) combined with UV or O₃ lead to enhancement in bacterial inactivation by 0.5–2.0 log units (Cho et al., 2011; Cho and Yoon, 2006; Lanao et al., 2008; Rubio et al., 2013).

5.2.2. Contaminant sequestration

Organic and inorganic micropollutants (such as endocrine disrupting chemicals, heavy metals, nitrate and arsenic) are prevalent in many water sources and in treated wastewaters which otherwise might be recycled. CDI, apart from removing inorganic salts by non-Faradaic means, may also contribute to the removal of these pollutants through a combination of Faradaic and non-Faradaic processes.

Arsenic is naturally present in groundwaters at concentrations ranging from less than 0.5 μg L⁻¹ to more than 5 mg L⁻¹ (Smedley and Kinniburgh, 2002). Groundwaters exhibiting arsenic concentrations well above the World Health Organization (WHO) guideline value for drinking water of 10 μg L⁻¹ (Edition, 2011) have been found in Argentina, Chile, Mexico, China and Hungary and, more recently, in West Bengal (India), Bangladesh and Vietnam (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). As(III) and As(V) are the predominant arsenic forms in natural waters with the former being more toxic than the latter (Pous et al., 2015). As most arsenic sequestration technologies are not very effective in directly removing the dominant uncharged As(III) species, pre-oxidation of arsenic sequestration technologies are not very effective in directly oxidizing and electrosorption (Fan et al., 2016; Garrido et al., 2009; Suzuki, 2002; Smedley and Kinniburgh, 2002). As(III) and As(V) form the key performance parameter in this analysis.

As reported by Fan et al. (2016), As(III) can be anodically oxidized to As(V) followed by electrosorption of the in-situ formed As(V) onto the surface of the anode. Following charging at 1.2 V for 120 min, the arsenic concentrations decreased from 50, 100 and 200 mg L⁻¹ to 2.3, 9.6 and 42.3 mg L⁻¹, respectively, with arsenic present in the treated water predominantly as As(V). It should be noted that in practical groundwater cases, arsenic coexists with other inorganic anions (and associated cations) with the concentrations of these inorganic anions (e.g., Cl⁻, NO₃⁻ and SO₄²⁻) several magnitudes higher than arsenic. As such, the impact of the presence of other inorganic salts on removal of arsenic by CDI from solution requires careful attention.

In addition to removal of salt and minor components from groundwaters, consideration has also been given to treatment of municipal wastewater effluents. These wastewaters typically contain a range of organic compounds with the chemical oxygen demand (COD) of these effluents ranging from ~20 to ~100 mg L⁻¹ as well as inorganic salts at concentrations ranging from ~100 to 1000 mg L⁻¹ (Kim et al., 2008; Li et al., 2011). Recently, Duan et al. (2015b) employed CDI for the simultaneous removal of phenol and NaCl from a synthetic wastewater. The anodic oxidation of phenol was achieved in the CDI system through (i) the direct oxidation of phenol at the anode, generating benzoquinone and catechol by hydroxylation and/or (ii) the indirect miniaturization by active chlorine which was generated through the anodic oxidation of Cl⁻ (Eq (4)) with the formation of chlorophenols as intermediate in this pathway. These aromatic intermediates were then oxidized to carboxylic acids and, ultimately, to CO₂. In a similar manner, Liu et al. (2016) confirmed that CDI was capable of breaking down naturally occurring humic substances via anodic electrochemical oxidation with subsequent electrosorption of oxidized humic substances and their derivatives. This indicated that CDI technology may be of use in the pre-treatment of drinking waters as it can decrease the extent of formation of disinfection by-products by partial removal of natural organic matter precursors.

While several attempts have been made to remove heavy metals including Cu(II) (Huang et al., 2014), Cd(II) (Huang et al., 2016), Pb(II) (Yang et al., 2014), and Fe(III) (Li et al., 2010), from waters by CDI, little mechanistic insight has been obtained with both non-Faradaic electroseparation and cathodic reduction of cations expected to be of importance for the fixation of these heavy metals. Huang et al. (2016) investigated the electro-enhanced removal of Cu(II) from water using a CDI cell equipped with activated carbon electrodes. When a low charging voltage of 0.4 V was applied, Cu(II) appeared to be removed from solution via non-Faradaic processes with no apparent deposition of elemental Cu on the cathode surface. During charging at 0.8 V, particles of 1–2 μm in size appeared on the electrode surface. On further increase in charging voltage to 1.2 V, large numbers of particles were generated and covered a significant portion of the electrode surface. XPS analysis revealed that these particles were a combination of metallic copper (i.e., Cu(0)) and cuprous oxide (i.e., Cu₂O), confirming the occurrence of cathodic reduction of Cu(II) at relatively higher charging voltages.

6. Perspectives and outlook

Faradaic processes in CDI systems have attracted increasing interest in recent years with investigation of both oxidation and reduction reactions resulting from application of charging potential leading to a firmer understanding of both the benefits and pitfalls of Faradaic effects. Here, we provide a comprehensive review of Faradaic reactions in CDI systems with particular attention given to catholic oxygen reduction and anodic carbon oxidation. One approach to gaining a perspective on the occurrence and impacts of CDI Faradaic reactions is to utilize a flowchart as described in Fig. 9 with these reactions playing an important role in (i) mitigation or elimination of the undesired Faradaic reactions in the system, (ii) employment of particular reactions which can be useful for improving desalination performance or achieving CDI multifunctionality (e.g., disinfection and micropollutant sequestration) and (iii) enhancement of Faradaic reaction-mediated desalination based on pseudopacapcitative effects. Charge efficiency in achieving particular water quality and water recovery rate targets is used as the key performance parameter in this analysis.

Carbon electrode oxidation caused by Faradaic reactions is one of the most critical issues in CDI long-term operation with these reactions resulting in carbon electrode deterioration and desalination performance decline. Use of membrane CDI (MCDI) appears to be effective in eliminating cathodic oxygen reduction with an associated positive shift in electrode potential to the anode thereby reducing the rate and extent of carbon anode oxidation with resultant extension of electrode lifetime. Combining ion-exchange polymers with carbon electrodes may also contribute to mitigation of carbon oxidation as well as alleviating resistance and ion-exchange membrane cost issues that are associated with MCDI. More detailed studies on this issue are required in order to refine the replacement of ion-exchange membranes by carbon-polymer composite electrodes.

There are very few examples showing that anodic chloride oxidation occurs in CDI systems with resultant production of active chlorine species that could be applied to in-situ disinfection or indirect oxidant of organic pollutants. This reaction is likely to occur in hybrid CDI systems equipped with both transition metal containing materials and carbon materials as electrodes, where unequal potential distribution and/or metal catalytic properties favor the oxidation of chloride at the anode. One major concern is that
the chloride oxidation process is likely to yield chlorinated byproducts, potentially increasing the health hazards associated with drinking water purification using CDI. In such systems, monitoring the possible formation of chlorine by-products such as chlorate, perchlorate, or organochlorine as well as oxidative products of the anion exchange membrane is recommended, especially when using higher voltages for drinking water desalination.

Cathodic oxygen reduction, considering that the cathode potential is always expected to be lower than the redox potential of the oxygen reduction reaction, will inevitably occur in CDI systems. Our recent findings have revealed that the dissolved oxygen concentration can serve as a simple and convenient indicator of the rate and extent of oxygen reduction. A mechanically-based kinetic model of the Faradaic reactions occurring at the cathode has been developed and found to satisfactorily describe the variation of DO consumed and H2O2 generated during CDI operation (He et al., 2016). The presence of H2O2 could provide the means of inducing disinfection or micropollutant degradation in the CDI system provided that H2O2 can be effectively activated to more powerful oxidants (by, for example, UV photolysis or O3 addition).

pH fluctuation is another serious issue in CDI systems as it affects the treated water quality and potentially results in scaling issues at the cathode if large amounts of alkaline earth metal ions such as Ca2+ or Mg2+ are present. Although we have demonstrated that Faradaic reactions contribute greatly to the pH fluctuations in CDI system with carbon electrodes, non-Faradaic processes such as the differing transport and adsorption/desorption rates of protons and hydroxyl ions may also play non-negligible roles. The contribution of Faradaic and non-Faradaic processes to pH fluctuations should be elucidated as this will assist in developing feasible strategies to mitigate any side effects. Additionally, in-situ measurement (e.g. by use of pH micro electrodes) or modelling of the pH variation at/near the electrode interface is required as this will enable further exploration of the mechanisms contributing to pH fluctuations.

To date, most attention has focused on non-Faradaic processes (i.e., capacitive ion storage in EDLs) in CDI with limited attention given to Faradaic processes despite the importance of these processes to both treated water quality and long term stability and performance of this technology. As such, some urgency exists with regard to improving our mechanistic understanding of Faradaic reactions with the goal of effectively mitigating the negative effects of these processes whilst taking advantage of their positive effects.

It is encouraging to see that Faradaic capacitive electrodes can contribute significantly to the enhancement of desalination performance through intercalation effects. Unlike the traditional carbon electrodes that take advantage of the pure EDLs for ion removal, Faradaic capacitive electrodes can remove ion species through Faradaic reactions with high efficiency and low energy consumption. Most recently, ultra-high salt removal capacity of more than 100 mg g⁻¹ was achieved when using these intercalation electrodes, almost seven times higher than that of traditional static capacitive carbon electrodes. However, the stability of such electrodes (particularly associated with the electrochemical leakage of metal ions) is currently a major concern and an issue to which more attention should be paid. Furthermore, it is necessary to develop cost-effective, stable, and novel intercalation cathodes and anodes to meet the requirement of capturing multiple cations and anions from real saline waters.

7. Conclusions

In conclusion, a comprehensive overview of the types and mechanisms of Faradaic reactions, i.e., carbon electrode oxidation, chloride oxidation, dissolved oxygen reduction, and Faradaic ion storage reactions that may occur in CDI systems has been presented here. The negative influences of these reactions on CDI lifetime and desalination performance has been described. A number of strategies such as optimization of cell configuration, modification of operational mode, and fabrication of novel CDI electrodes have been proposed to reduce (or even eliminate) Faradaic side effects. It is also recognized that Faradaic reactions have a variety of exciting and promising applications including the incorporation of intercalation electrodes for highly saline water desalination or value-added ion separation/recovery through reversible Faradaic reactions and employment of particular reactions enabling CDI to fulfil its promise of multifunctionality (including disinfection and micropollutant sequestration).