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Improving the feasibility and applicability of flow-electrode capacitive deionization (FCDI): Review of process optimization and energy efficiency

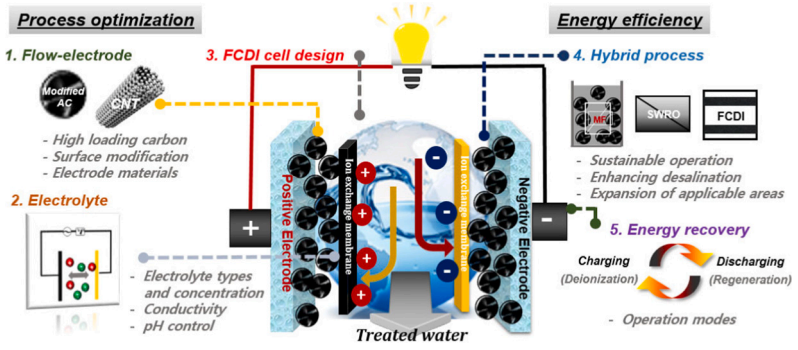
Yong-Uk Shin [a], Jihun Lim [a], Chanhee Boo [b,*], Seungkwan Hong [a,*]

[a] School of Civil, Environmental, and Architectural Engineering, Korea University, Seoul 136-701, Republic of Korea
[b] Water Cycle Research Center, National Agenda Research Division, Korea Institute of Science and Technology (KIST), Seoul 02792, Republic of Korea

HIGHLIGHTS

- Comprehensive review of recent advances in flow-electrode capacitive deionization (FCDI)
- FCDI process optimization to improve desalination efficiency
- Critical energy analysis in comparison with existing desalination technologies
- FCDI in desalination, softening, nutrient recovery, and toxic metal removal
- Future research directions for expanding practical application of FCDI

GRAPHICAL ABSTRACT



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ABSTRACT

Flow-electrode capacitive deionization (FCDI) is a new electrochemical-based desalination technology that addresses the limitations of preceding CDI processes through the use of a stationary carbon electrode and ion-exchange membrane. As with conventional CDI configurations, non-Faradaic reactions (i.e., ion electrosorption) of the electric double layer model is the principal ion separation mechanism of FCDI. This technology also offers the unique ability for continuous ion/salt separation by circumventing constraints with electrode saturation. This paper reviews recent advances in FCDI, discusses the feasibility and applicability of this technique, and suggests potential niche applications for saline water/wastewater treatment and resource recovery. Additionally, it also critically discusses factors that deteriorate FCDI performance, operating conditions, process energy efficiency, and optimization of the electrode, electrolyte, and cell design. The insights from this review will shed light on directions for future FCDI research and inform the implementation of FCDI technology.

1. Introduction

The threat of water scarcity continues to grow around the world due to rapid industrialization, climate change, and the proliferation of source water contamination. Sustainable exploitation of alternative water resources is now essential to enable safe and adequate water supply in many countries. The desalination of saline water is considered a key solution due to easy source water accessibility and the high

* Corresponding authors.
E-mail addresses: chanhee.boo@kist.re.kr (C. Boo), skhong21@korea.ac.kr (S. Hong).

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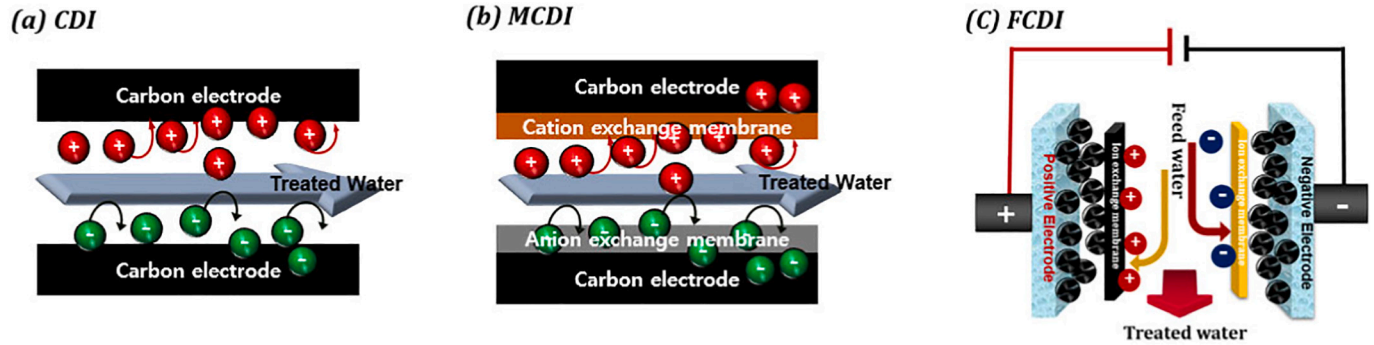

Fig. 1. Schematic of (a) capacitive deionization (CDI); (b) membrane-capacitive deionization (MCDI); and (c) flow-electrode capacitive deionization (FCDI).

freshwater production capability [1–3]. Various desalination technologies have been developed in recent decades, including thermal-driven multi-stage flash (MSF) distillation [4], multiple effect distillation (MED) [5], pressure-driven seawater reverse osmosis (SWRO), and electro-driven capacitive deionization (CDI). Thermal-driven MSF and MED consumes large amounts of energy to achieve water vaporization for freshwater production. In contrast, reverse osmosis (RO) technology is known to be less energy intensive due to the membrane-based separation mechanism driven by hydraulic pressure. The earlier SWRO plants were reported to operate at approximately 20 kWh/m^3 of specific energy consumption (SEC) [2], whilst current state-of-the-art SWRO plants only consume ~3 kWh/m^3. This is a result of significant improvements in process design, including the development of high-performance RO membranes, the installation of an energy recovery device and the use of more energy-efficient pumps [6–8]. Despite this progress, the RO process still suffers from other critical problems such as high capital costs, membrane fouling in long-term operation, and a need for intensive pre-treatment [9].

Capacitive deionization (CDI) is an electrochemical-based desalination technology with potential niche applications in which this technology is able to outperform the RO process. A typical CDI process uses a porous carbon electrode to capture charged ions and desalinate the water [10–12]. The CDI desalination mechanism is based on the electrical potential gradient over two charged electrodes; this may be explained by the electrical double layer (EDL) model. CDI operates at a relatively low charging voltage of <1.2 V to prevent faradaic reactions; these are oxidation-reduction reactions that occur at the surface of the electrode [13]. Such low voltage conditions, together with process operation without hydraulic pressure and relatively easy fouling control of the electrode, renders CDI a low-energy desalination method. Membrane capacitive deionization (MCDI) has been developed and widely explored, whereby the process incorporates ion exchange membranes (IEMs) between two electrodes in the CDI configuration. The ion adsorption capacity of MCDI is higher than conventional CDI with better charge efficiency due to increased ion selectivity through ion exchange membranes [11,14]. However, the desalination performance of MCDI continues to be limited by electrode saturation as charged ions are stored in the micro and macro-pores of the fixed electrode [14,15]. As a result of this limitation, MCDI is only applicable to treat low to moderate ion concentrations of approximately 3000–4000 mg/L [9]. Additionally, the continuous operation of the MCDI process is constrained due to the unavoidable regeneration of the ion-saturated electrode [16,17].

The flow-electrode capacitive deionization (FCDI) process has recently been proposed as a means to address the limitations of MCDI [18]. FCDI uses a slurry-type electrode, these contain typically small particles of activated carbon sized at ~10 μm with a high specific surface area of ~3200 m^2/g, leading to higher electrosorption capacity (>20 mg of NaCl per gram of carbon particles) compared to MCDI (average 1–11 mg/g) [19]. The high specific surface area of flow electrodes in FCDI enables effective ion separation and the desalination of highly saline feed water. Some studies have demonstrated the potential of FCDI to desalinate feed water with high total dissolved solids (TDS) concentrations up to the level of seawater (i.e., ~35,000 mg/L) [16,20]. As opposed to conventional CDI and MCDI, FCDI enables continuous charge–discharge operations through an external ion desorbing system. In this system, the discharged flow electrodes from the anodic and cathodic chambers are mixed and regenerated, which means that FCDI desalination is easily scalable simply through an increase in the amount of flow-electrodes [18]. These advantages highlight the potential for FCDI to be implemented for industrial-scale desalination plants [10,18]. Suspended carbon particles (i.e., flow electrodes) in FCDI pass through a flow channel on the current collector. When a voltage is applied, charged ions are transported across the ion exchange membrane and adhere to the surface of suspended carbon electrodes. Importantly, FCDI is driven by a relatively low electric potential of <1.2 V, where additional energy is only required for the circulation pump; this trait emphasizes its substantial potential for energy-efficient desalination [13].

From the advent of FCDI in 2013, a total of 71 papers on FCDI have been published in a range of subjects. To date, most studies have focused on FCDI cell architecture design (32.39%), followed by the development of carbon electrode materials (26.76%). Remaining research on FCDI have primarily dealt with process applicability (23.94%) and energy efficiency (9.85%). The initial research involved largely investigating the improvement of ion separation efficiency by designing advanced carbon electrodes and increasing the carbon electrode loading in the flow cell. From 2016, the research focus shifted to the design of flow cell configuration and operation, followed by the most recent research on the practical applications of FCDI. Beyond the foundational and lab-scale investigations on FCDI, it is particularly important to critically assess the feasibility of this technology for various industrial applications.

This paper provides a comprehensive review of FCDI technology, focusing on the recent advancements in suspended carbon electrodes, electrolytes, and cell systems. We provide a critical analysis of process optimization and hybridization, which may enhance desalination performance and the energy efficiency of FCDI. We highlight recent efforts to improve the feasibility of FCDI across many industrial applications based on the inherent advantages and recent advancements of this electrochemical-based separation process. This includes applications such as desalination, softening, decontamination, and resource recovery. As such, this review is timely as it offers guidelines for future research and contributes to practical applications of FCDI.

2. Comparison of FCDI with conventional and membrane-CDI

The function of all electro-driven desalination processes (i.e., CDI, MCDI, and FCDI) are primarily based on the non-faradaic reaction of the electrical double layer (EDL) model, where two porous electrodes separate and store ions from feed water through electrosorption [11,21,22]. However, FCDI has three key advantages over the

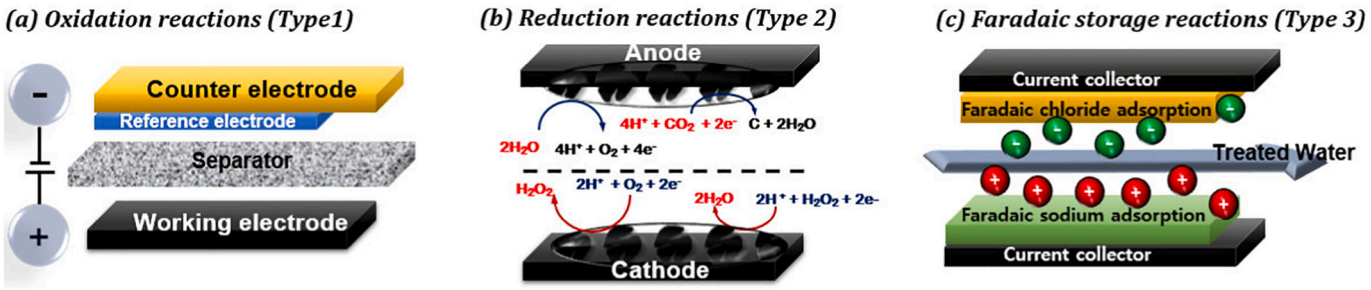

Fig. 2. Schematic of various faradaic reactions in CDI process.

conventional CDI and MCDI: (i) the potential for continuous desalination with the regeneration of the flow electrodes in an external reservoir; (ii) improved ion adsorption capacity (or, improved desalination efficiency); and (iii) the potential for energy production during flow electrode regeneration. A schematic of the FCDI process is shown in Fig. 1, comparing this process to conventional CDI which uses a stationary carbon electrode and MCDI equipped with ion exchange membranes [18].

2.1. CDI and MCDI mechanisms

Ion separation and storage during CDI desalination may be achieved by two main electrochemical mechanisms [23,24]. Non-faradaic reactions, the most common phenomenon in electrochemical-driven separation, are mainly based on the formation of EDL at the surface of the porous carbon electrode. Specifically, ions are separated from saline water and stored in the diffusive layer within the porous electrode structure [14,25]; this phenomenon is referred to as electrosorption and normally occurs at an electric potential <1.2 V.

The other CDI mechanism of faradaic reactions produces negative and positive impacts on ion separation efficiency. The four key negative impacts include (1) a decrease in desalination performance and energy efficiency, (2) the reduction of electrode lifespan, (3) the formation of chemical by-products, and (4) pH fluctuation in the product water [26,27]. The positive impacts of faradaic reactions include improving the desalination process by forming valuable reactive species (i.e., HOCl, OCl^-, and H_2O_2) through pseudo-capacitive intercalation effects [28].

Fig. 2 illustrates the three different types of faradaic reactions that take place during CDI desalination [29–31]. Type 1 is the oxidation of carbon, chloride, and water, which occur on the anode side (Fig. 2a). Among these oxidation reactions on the anode side, carbon electrode oxidation impairs its pore structure, resulting in ion adsorption capacity loss [26,32]. The type 2 oxygen reduction on the cathode side generates an asymmetric potential between the two electrodes [33]. Reaction by-products, such as H_2O_2, produced during the reduction of oxygen may be used for water disinfection or as a radical for advanced oxidation. Cathode reduction also results in the precipitation of heavy metals present in the feed water [34]. Type 3 is pseudo-capacitive/intercalation effects that occur during faradaic storage, where ions are captured in the electrode by reversible redox reactions. These effects differ from the storage in EDLs at interfaces between the electrode and electrolyte [27,35–37].

CDI and MCDI technologies share the underlying electrochemical mechanisms of faradaic and non-Faradaic reactions, with the key difference being that the latter deploys IEMs in front of the electrodes to improve desalination performance by allowing the selective transport of counter ions (i.e., ions with the opposite charge to the membrane) over the co-ions [38–40].

2.2. FCDI mechanism

FCDI desalination uses slurry-type suspended electrodes that travel between two oppositely charged electrodes in fluid flow. This unique configuration of flow electrodes means that FCDI has the potential to treat relatively high saline feed waters (i.e., TDS concentrations of 35,000 mg/L) in continuous operation mode. The FCDI system includes a curved flow channel to enable the migration of electrodes in the feed water across the current collector. Here, the simultaneous desalination of saline water and the production of current through the IEM is achieved. As such, the operational conditions play a critical role in FCDI desalination performance; these conditions include electrode particle size, carbon weight percentage, and the type and concentration of an aqueous electrolyte [16,41,42]. For instance, small-sized particles facilitate ion migration inside their porous structure across the total pore volume with a short diffusion pathway [43]. The electrical conductivity of flow electrodes is also dependent on their carbon weight percentage, where a higher carbon weight percentage yields better desalination performance [44]. The electrolyte concentration is another important factor impacting upon FCDI performance. Experimental investigations have shown that FCDI desalination efficiency peaks at 2.44 wt% of salt content in the electrolyte [16,41]. The diverse range of potential operating factors have inspired researchers to analyze FCDI desalination efficiency from different systems, such as flow electrode-based energy storage systems, redox flow electrodes, and electrochemical flow capacitors. The main electrochemical separation mechanism of FCDI is the non-faradaic reaction as the adsorption of ions on the flow electrode takes place within the non-faradaic voltage range (<1.2 V) [18]. However, faradaic reactions have also been reported to occur through charge exchange at the electrode/electrolyte interface as the major constituent of the flow electrode is an electrolyte of ionic composition [45,46].

3. Optimization of the FCDI process

Despite the potential for FCDI as a continuous and scalable desalination process, there is a critical need for further studies on optimizing the carbon electrode, electrolyte, cell design, and operating conditions. Typically, flow electrodes are prepared from activated carbon-based materials. As such, FCDI energy efficiency is heavily dependent on ion electrosorption capability of activated carbon (AC) electrodes, the characteristics of aqueous electrolytes, and flow cell design. This section systematically reports on the optimization of these key process features to improve the desalination capability and energy efficiency of the FCDI system.

3.1. Flow electrodes

3.1.1. Current types of FCDI electrode materials

In FCDI, conventional stationary carbon electrodes are replaced by small electrode material particles suspended in a solution containing electrolytes [41]. Previous research has used flow electrodes in the form of slurry as an electrodialysis device; this is fundamentally the same concept as FCDI. A number of studies have investigated the electrochemical polarization dynamics of activated carbon and graphite flow electrodes [47,48]. Recent research has also utilized flow electrodes in

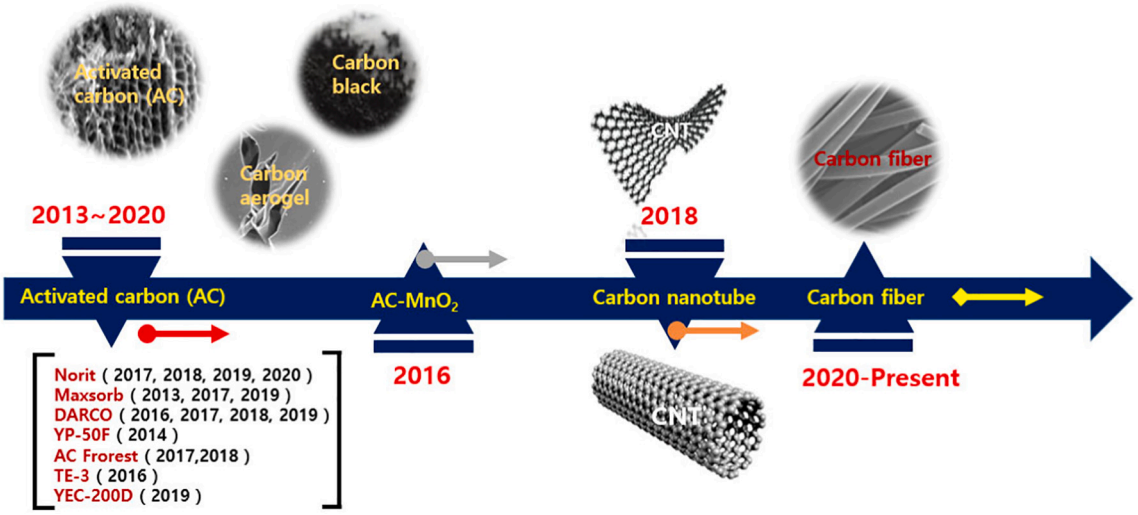

Fig. 3. Historical development of various carbon-based electrode materials for FCDI.

an electrochemical flow capacitor system where the solution flows through the unit for continuous ion adsorption/desorption [49].

Fig. 3 presents the historical development of carbon-based flow electrode materials for FCDI (typically sized at ~10 μm), including activated carbon particles, carbon aerogel, AC-MnO_2, carbon nanotubes (CNTs), and carbon nanofibers (CNFs) [17,50–53]. Among the various carbon-based materials, AC is considered the most suitable flow electrode material characterized by a high surface area, low cost, and easy processability [54–56]. The ion separation efficiency in FCDI is largely dependent on the properties of AC electrodes, such as average particle diameter, total pore volume, specific surface area, and surface chemistry [20]. Furthermore, all AC electrode characteristics are closely related to the operation parameters of mass loading, and the electric and fluidic resistances of the flow electrodes. This means that understanding the relationship between the AC electrode properties and FCDI process parameters is important to optimize performance stability, energy efficiency, and product water quality [57].

Recent FCDI studies have used various types of AC carbon electrodes provided by different manufacturers. Norit SX Ultra Activated Charcoal (25%) and 100-mesh Darco Activated Charcoal (25%) are the two most frequently used AC electrodes in FCDI studies, this is followed by Maxsorb MSC-30 (Kansai Coke and Chemicals Co. Ltd., Japan) (10%). The specific surface areas of common AC electrode materials are mainly between 1000 and 1500 m^2/g, as reported in recently published FCDI research. Whilst there is a general consensus that high specific surface area enables an increase in the ion adsorption capacity, the type of AC electrodes used in FCDI research is also determined based on the material cost, morphology, and size of the AC [41]. The combined flow electrodes of dilute slurry and densely fluidized AC that have been proposed more recently have been shown to enhance electrical conductivity. However, attention needs to focus on determining the combination of AC types in terms of morphology, the effects of gravity and electrical charge. Although the AC electrode is a major constituent of FCDI and as such, mainly determines desalination performance, there is currently an absence of systematic research that demonstrates the dependence of the AC electrode properties on the deionization capability of FCDI. Furthermore, a reasonable standard needs to be established for AC electrode selection; this would be very helpful in enhancing the FCDI process.

3.1.2. *Challenges associated with FCDI electrode materials*

FCDI uses a slurry-type electrode of AC flowing in the electrolyte. In a simple solution of deionized water with typical electrolytes such as dissolved NaCl, the flow electrical resistance of the solution is considered very low. The AC particles flowing in the electrolytes induce a non-homogeneous mixture condition, causing non-negligible electrical conductivity of ~0.1–1 mS/cm [58,59]. When flow electrodes (i.e., AC particles) are in contact with the current collector, electrons transfer from the current collector to the electrode. For this reason, the conductivity of the flow electrode in FCDI is lower than a stationary electrode in conventional CDI [41]. This means the charge transport in FCDI is mainly constrained by the high electrical resistance of the flow electrodes, limiting the salt adsorption rate and energy efficiency.

There are two main goals in terms of developing high-performance AC electrodes in FCDI; (i) higher loading capacity, and (ii) reduced impact on electrolyte viscosity to decrease the required pumping energy and incidence of operational problems. The simultaneous achievement of these goals is highly challenging as increasing the carbon mass loading results in an increase in the suspension viscosity. To address this paradox, studies have focused on strategies to overcome the limitations of carbon materials via oxidative/surface modification, surfactant addition, and novel reactor designs [20,44,60].

One previous study used an emulsion polymerization method to attempt the surface modification of activated carbon particles in order to cover the particle surface with ion-exchange polymers. The cathodic and anodic flow electrode solutions were prepared separately. Specifically, the cathodic flow electrode was coated with a polymer with sulfonate groups ($-SO_3^-$), whilst the anodic flow electrode was modified using a polymer with trimethylammonium groups ($-N^+(CH_3)_3$). Researchers undertook rheological analysis of the solutions with these surface-polymerized flow electrodes across a range of carbon mass loadings and compared the results with those using conventional AC. The results varied for the cathode and anode electrodes, although both had successfully achieved a significant decrease in solution viscosity. Compared to conventional AC, the anode flow electrode reported a solution viscosity that was less than one-third of the conventional AC flow electrode at a carbon mass loading that was more than twofold. For the cathode flow electrode, a similar solution viscosity was observed when the carbon mass loading of synthesized carbon was more than twofold that of conventional AC. This improvement was attributed to the reduced hydrophobicity between the AC particles as their outer surface contained functional groups (i.e., $-SO_3^-$ and $-N^+(CH_3)_3$), which imparted surface hydrophilicity. The difference in viscosity of the two flow electrodes was associated with the extent of surface modification [20].

Another study used oxidative methods to prepare granular AC with heteroatom surfaces. A wet oxidation method using nitric acid was used to cover the AC surface with oxygen heteroatoms. Rheological analysis results confirmed that the increased surface hydrophilicity of the

Table 1
Average salt adsorption rate (ASAR) of FCDI evaluated at different operating cell modes and with surface-modified flow electrodes.

Feed water TDS conc. (mg/L)	Flow rate (mL/min)	Average salt absorption rate (mg/(min·cm^2))	Operating mode	Electrode carbon type	Carbon conc. (wt %)	Electrolyte NaCl conc. (mg/L)	Flow rate of carbon electrode (mL/min)	Remarks	Ref.
35,000 (NaCl solution)	3	0.010	CV mode, 1.2 V	BEAPS-AC0830 (Spherical AC)	9.1	0	25	Correlation between NaCl concentration of electrolyte and salt removal efficiency	[16]
		0.018				5000			
		0.022				15,000			
		0.023				25,000			
		0.024				35,000			
		0.024				45,000			
		0.025				55,000			
		0.025				65,000			
		0.025				75,000			
35,000 (NaCl solution)	3	0.025	CV mode, 1.2 V	Spherical AC (BEAPS-AC0830; Asahi Organic Chemicals, Japan)	11.11	35,000	25	Analysis of desalination performance of SCC-FCDI	[62]
		0.027			11.11				
		0.021			9.09				
		0.017			6.98				
35,000 (NaCl solution)	3	0.012	CV mode, 1.2 V	BEAPS-AC0830 (AC)	9.1	25,000	25	Enhancing desalination performance by surface-modified carbon electrodes	[20]
		0.011		BEAPS-AC0830 (AC-N/AC-S) surface modified AC particles	16.7				
		0.023			20				
		0.037			23.1				
		0.037			25.9				
5000 (NaCl solution)	5	0.093	CC mode, ~2.65 V	YP-50F activated carbon	28	10,000	5	Improvement in energy efficiency of oxidized carbon materials for FCDI electrodes	[60]
		0.065		YP-50F activated carbon oxidized			5		
		0.095	CC mode, ~1.48 V	YP-50F activated carbon			13		
		0.082		YP-50F activated carbon oxidized			13		
		0.078	CC mode, ~0.74 V	YP-50F activated carbon			23		
		0.069		YP-50F activated carbon oxidized			23		
1168.8 (NaCl solution)	0.5	N.A.[a]	CV mode, 1.6 V	TE-3 activated carbon beads	35	1168.8	2.5	Increasing carbon concentration (up to 35%) for improved desalination performance	[41]

[a] N.A.: Not Available.

heteroatom-modified carbon particles reduced solution viscosity by 70–80%, compared to the solution prepared with simply oxidized or unmodified-AC particles. The results were equally attributable to the decrease in hydrophobic interactions between the AC particles due to the increase in their surface hydrophilicity. In addition, surface charge imparted by oxygen heteroatoms was considered an additional factor inducing a repulsive force between AC particles, allowing higher particle dispersibility, and increasing the carbon mass loading and decreasing solution viscosity [60].

Modifying the surface of the flow electrode by surfactants may also be an effective strategy to increase the loading capacity of FCDI. Surface-grafted surfactants are amphiphilic compounds that effectively lower the interfacial tension between flow electrode materials and the surrounding solvent. This increases the dispersion of flow electrodes in solution, reducing the overall viscosity. The modified arrangement of atoms surrounding the electrode material also induces repulsive reactions when the electrical layer/electron clouds overlap with those of other electrode materials. This repulsion is known as a "steric hindrance", suppressing the aggregation of electrode materials, and enabling further reductions in solution viscosity [61]. A previous study that had adopted such a method utilized four different types of surfactants; among these two drastically reduced the solution viscosity following grafting [61].

The design of a novel reactor is another method to increase the carbon mass loading for improved FCDI performance. A fluidized bed reactor was recently introduced using relatively large-sized carbon particles (>100 μm diameter); this size is sufficiently large to be affected by gravity [41]. The flow electrodes were arranged in the reactor to have an upward flow, such that the carbon beads within the flow electrodes were impeded by gravity and their flow inside the channel was much slower compared to the surrounding solution, providing for a higher packing density of the electrode material. This novel design produced a 35% mass loading with no significant increase in solution viscosity [41].

The differences in the experimental conditions such as electrolyte NaCl concentration and flow channel dimensions, make it challenging to precisely analyze and compare the average salt adsorption rate from different studies. All experimental conditions, such as operating mode (i.e., constant current or constant voltage mode), the flow rate and TDS concentrations of the feed water, interactively affect the deionization rate. Most FCDI studies have used varying experimental conditions, where in some cases, they did not clearly state the details. To systematically compare FCDI performance based on various research, converged experimental conditions and a consistent unit of salt removal efficiency needed to be established [16,62]. The reported salt removal efficiency of FCDI had been expressed in various ways, such as (maximum) salt adsorption capacity (SAC) (mg/g), salt removal efficiency (SRE) (%) (calculated using Eq. (1)), and the average salt adsorption rate (ASAR) (mg/(min·cm^2)) (calculated using Eq. (2)):

$$\mathrm{SRE}\ (\%) = \left[\frac{C_i - C_f}{C_i}\right] \times 100 \tag{1}$$

where C_i and C_f are the initial and final salt concentrations in the feed water. The ASAR was expressed as:

$$\mathrm{ASAR}\ \left(\frac{\mathrm{mg}}{min \cdot \mathrm{cm}^2}\right) = \left[\frac{V \times \Delta c}{At}\right] \tag{2}$$

where V is the saltwater volume; Δc is the difference between the initial

Table 2
Evaluation of salt adsorption performance under various electrolytes and pH conditions.

Feed water TDS conc. (mg/L)	Flow rate (mL/min)	Average salt absorption rate (mg/(min·cm^2))	Applied voltage (V)	Electrode carbon type	Carbon conc. (wt %)	Electrolyte NaCl conc. (mg/L)	Flow rate of carbon electrode (mL/min)	Remarks	Ref.
650 (Na_2SO_4 solution)	11	0.037	0.6	Fuzhou Yuhuan AC	20	650 (Na2SO4 solution)	4	The effect of feed water concentration and applied voltage on desalination performance	[10]
		0.055[a]	0.9						
		0.075[a]	1.2						
30,000 (Na_2SO_4 solution)		0.028	0.6						
		0.065	0.9						
		0.1	1.2						
650 (Na_2SO_4 solution)	11	0.056	0.6		AC 20, CB 1				
		0.080[a]	0.9						
		0.120[a]	1.2						
30,000 (Na_2SO_4 solution)		0.031	0.6						
		0.075[a]	0.9						
		0.105[a]	1.2						
2000 (NaCl solution)	30	0.011	1.2	100-mesh DARCO activated charcoal	1	0	100	Enhancement of desalination performance using redox-active flow electrodes of hydroquinone (H2Q) and comparison with other types of electrodes	[19]
		0.015				180.15 (H2Q)			
		0.019				216.18 (H2Q)			
		0.027				252.21 (H2Q)			
35,000 (NaCl solution)	3	0.004	1.2	BEAPS-AC0830 (Spherical AC)	10	0 (mg/L)	25	Enhancement in desalination performance and cost reduction of FCDI process via the use of seawater as an electrolyte	[16]
		0.007				5000 (mg/L)			
		0.008				15,000 (mg/L)			
		0.009				25,000 (mg/L)			
		0.009				35,000 (mg/L)			
		0.009				45,000 (mg/L)			
		0.010				55,000 (mg/L)			
		0.010				65,000 (mg/L)			
		0.010				75,000 (mg/L)			
584.4 (NaCl solution)	5	0.001	1.2	Activated charcoal Norit	5	146.1	10	Influence of difference in ionic strength between the electrode and feed solutions on desalination performance	[64]
29,220		0.105							
58,440		0.230							
4000 (NaCl solution)	60	SAC 30 mg/g	1.2	NoritSX Ultra Activated Charcoal	5.26% (5 wt%)		60	Improvement in current efficiency (desalination) via preventing faradaic reactions through pH neutralization of seawater	[74]
		78%				After 22.5 h, 48.5 h HCl and NaOH solution input			
		100%				Initial 0.0316 M, HCl and NaOH solution input			
		58%				Initial 1 M, HCl and NaOH solutions input			

[a] Approximate value from the graph.

and final feed salt concentrations; A is the effective area of flow electrodes; and t is the time [63]. ASAR considers a range of FCDI operating conditions including cell architecture, electrode material, charging time, effective electrode sorption area, and the feed water characteristics. In order for these results to be comparable, we normalized the unit of SRE reported in FCDI studies based on the FCDI cell operational modes and surface-modified flow electrodes in Table 1. In Table 2, the salt adsorption rates were evaluated under different electrolyte compositions and pH conditions (refer to Section 3.2).

Considerable research effort has been directed towards developing AC materials via surface modification by targeting for an improved FCDI desalination performance. As summarized in Table 1, these newly synthesized flow electrodes show significant improvement in the SRE compared to conventional AC electrodes. A detailed illustration of these novel surface-modified electrodes is presented in Section 3.2.2. Whilst the observed lab-scale SAC of these flow electrodes has been impressive, their practicality in terms of industrial-scale installation requires examination [16].

Interestingly, one recent study evaluated a flexible membrane electrode assembly (MEA) produced from carbon fiber fabric current collectors laminated with thin ion-exchange membranes [53]. When compared with conventional graphite current collector, the carbon fiber MEA yielded equal salt transfer rates. This was because the thin ion-exchange membrane allowed a reduction in the potential drop, whilst the thickness of the graphite current collector was an inhibitor during operation.

3.2. FCDI electrolyte

3.2.1. Electrolyte characteristics (concentration and composition)

The non-homogeneous distribution of carbon-based flow electrodes with relatively low conductance in the electrolyte limits the achievable SAR and thus energy efficiency of FCDI. There are two ways in which to enhance the conductivity of the electrolyte without simply increasing the weight percentage of the flow electrodes. First, the electrolyte concentration has been increased to reduce the internal resistance from the flow electrodes. Second, the addition of a supplementary charged species such as conductive agents (i.e., carbon black) and electron mediators (i.e., H_2Q/Q couple) in the electrolyte to has enhanced charge transfer efficiency [16,19]. Despite potential higher electrolyte conductivity, the first option to increase electrolyte concentration may cause undesired ion diffusion to the feed water. Thus, the optimization

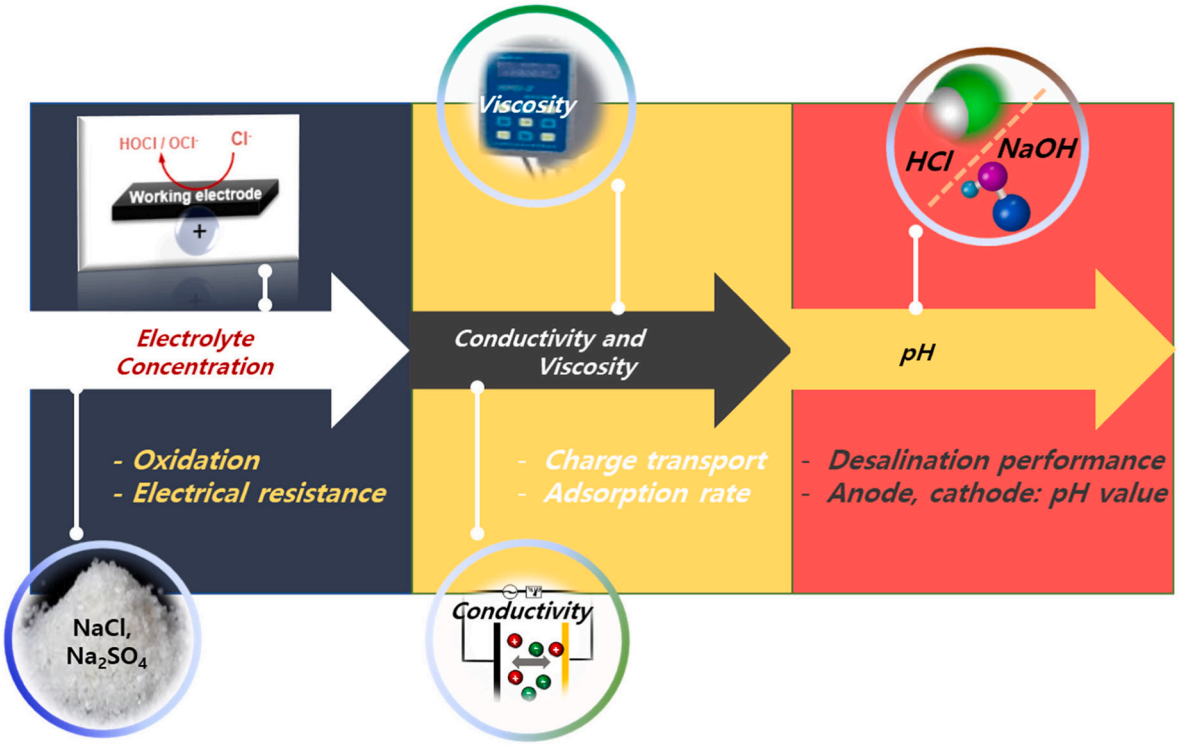

Fig. 4. Important operating parameters determining FCDI desalination performance.

of electrolyte concentration is required to achieve high desalination efficiency whilst preventing reverse ion diffusion (Fig. 4(a)). A meaningful relationship between electrolyte concentration and the ASAR has been demonstrated for the range of 0.004 mg/min·cm^2 with no NaCl electrolyte to 0.01 mg/min·cm^2 with 55,000 mg/L of NaCl electrolyte and an NaCl feed water concentration of 35,000 mg/L [16]. The desalination efficiency of FCDI drastically increased for electrolyte concentrations up to 15,000 mg/L NaCl, followed by a mild increase under higher electrolyte concentrations.

The electrolyte and feed salt concentration greatly affect long-term FCDI desalination performance. Complete charge-discharge reversibility in FCDI, such that an equal amount of ion had adsorbed and desorbed would not occur due to the concentration gradient between the electrolyte and the feed solution; this caused diffusive ion transport. The highest NaCl electrolyte concentration tested to date was 25,000 mg/L, although it is likely that even higher electrolyte concentrations may be utilized to treat feed water with higher salinities [16,64]. Maintaining a low salt concentration gradient between the electrolyte and the feed water has been observed to be beneficial to enhance FCDI performance [10]. However, although the addition of salts enhances ASAR, there are still two major concerns: (1) significant concentration polarization due to a large concentration difference between the electrolyte and feed water at the membrane surface; and (2) the subsequent inorganic salt precipitation on the membrane surface.

The addition of conductive agents or electron mediators in the electrolyte also improved charge transfer efficiency and the desalination performance of FCDI. Conductive agents such as carbon black powder (CB) have been shown to increase FCDI desalination efficiency from 0.075 to 0.120 mg/min·cm^2 by decreasing the internal resistance of flow electrodes. There are also reports of a subsequent reduction in the energy consumption of the FCDI process with CB conductive agents [10]. The presence of electron mediators such as hydroquinone (H_2Q) and benzoquinone (Q) in the electrolyte has also been demonstrated to enhance charge transfer efficiency. These electron mediators facilitate the redox transformation; as such, the application of multi-electron organic redox molecules is able to increase the capacitance of flow electrodes through pseudo-capacitive effects [65,66]. Transitory inner-sphere storage of quinoid molecules allow for the transfer of electrons to the collector surface. Then, aqueous H_2Q is oxidized to Q on the positively charged current collector in the anodic chamber [67,68]. The addition of 252.2 mg/L of H_2Q in the electrolyte has been found to increase the ASAR from 0.011 to 0.027 mg/min·cm^2 [19,23]. Based on these preliminary findings, future research should be directed at identifying a greater number of effective conductive agents and electron mediators, such as redox compounds, to further increase the ASAR of FCDI [69].

Table 2 summarizes recent research to improve the salt adsorption rate and charge efficiency of FCDI by optimizing the electrolyte and using conductive agents or electron mediators. Most studies employed NaCl salts for the electrolyte and feed water [16,20,41,44,60,70,71]. Further evaluation of the FCDI separation efficiency for diverse species is required through the use of different types of electrolytes, as opposed to simple NaCl. Studies have focused on how existing monovalent or divalent ions in the electrolyte and the feed water effects salt removal performance and fouling. Furthermore, ions migrate in both directions between the feed water and the flow electrode based on the chemical potential gradient. This phenomenon requires the careful observation of chemical transference to prevent the inflow of toxic chemicals into the feed solution during the addition of new chemicals as conductive agents or electron mediators. Thus, the ongoing development of FCDI technology utilizing seawater as the electrolyte is viable [16].

3.2.2. *Electrolyte conductivity and viscosity*

The electrical conductivity of the FCDI electrolyte is strongly dependent on the carbon weight percentage (CWP, wt%) of the flow electrode [41,44]. Increasing the flow electrode loading enables more effective electric charge transport with higher electrolyte conductivity (Fig. 4(b)) [20,60]. However, the practical CWP of flow electrodes cannot exceed 20 wt% to prevent clogging within the FCDI flow cell, arising from the physical properties of the carbon-based micro-particles [41]. Low viscosity carbon beads are relatively free from clogging and, as such, typically demonstrate better FCDI performance.

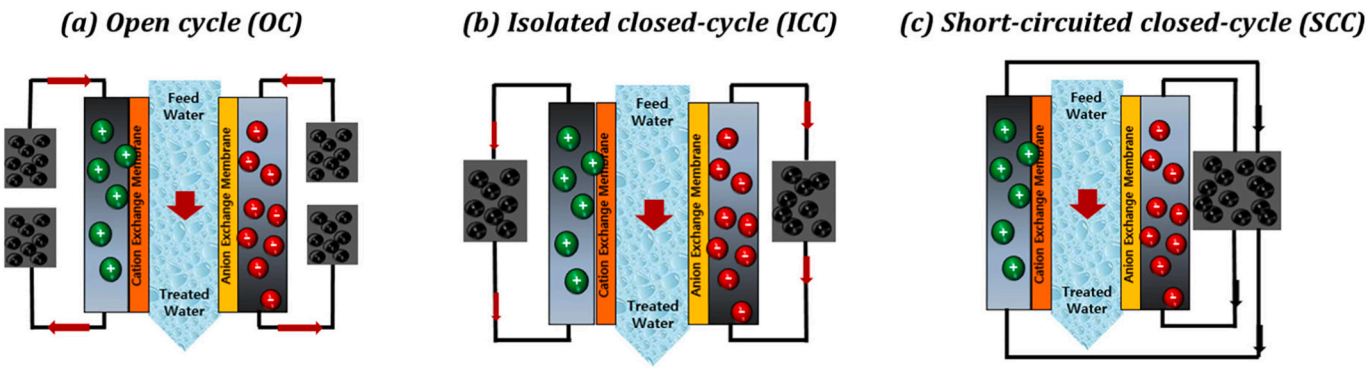

Fig. 5. Schematics summarizing the different flow electrode operation modes.

One possible means to raise flow electrode loading without significantly increasing the electrolyte viscosity is applying surface-modified AC electrodes. These surface-modified AC particles with ionic headgroups are homogeneously dispersed in the electrolyte and are able to marginally influence electrolyte viscosity. Tailored surface functionality with specific ionic groups may also enhance the ion adsorption rate by increasing the repulsion of co-ions [72,73]. Table 1 shows that surface-modified spherical AC with trimethylammonium (AC-N) for the anode and with sulfonate (AC-S) for the cathode enabled the application of high CWPs of 23.1 and 25.9 wt%, respectively, in the electrolyte. This produced a higher desalination efficiency of 0.037 mg/min·cm^2, whilst the conventional CWP was limited to 20 wt%. A polymer with ion-selective functional groups acts as a dispersant, inducing electrostatic repulsion between AC particles, resulting in a homogeneous dispersion of flow electrodes in the electrolyte [41]; the maximum ASAR of 0.037 mg/min·cm^2 was achieved with this functionalized polymeric dispersant. The reported ASAR indicates a significant improvement compared to the 0.025 mg/min·cm^2 obtained when using an unmodified carbon electrode under identical experimental conditions. This difference clearly demonstrates the enhanced desalination performance of the surface-modified AC electrodes [16,62]. Chemically oxidized AC also enables high flow electrode loadings in FCDI. The surface-oxidized AC with improved hydrophilicity exhibited better flow dynamics and dispersibility in the electrolyte. The aggregation of AC particles decreased due to reduced hydrophobic interactions caused by surface oxidation. A surface-oxidized AC loading in the electrolyte that was as high as 28 wt % was found to render an ASAR of 0.095 mg/min·cm^2 [16,60,62].

3.2.3. Electrolyte pH

When an electric potential is applied in the FCDI process, the pH of the electrolyte changes due to faradaic reactions on the surface of the anodic and cathodic flow electrodes. Despite the relatively low voltage applied in FCDI, the faradaic reaction continues to takes place [74]. The complex surface chemistry of AC particles with diverse functional groups accounts for the pH fluctuation during FCDI operation; this fluctuation deteriorates the desalination efficiency. Therefore, control of the electrolyte pH is a potential means of enhancing FCDI desalination performance (Fig. 4(c)) [16]. Adding appropriate amounts of HCl or NaOH to neutralize the pH of the cathode and anode electrolytes has been demonstrated to substantially increase the SAC of flow electrodes [74]. However, the addition of acids/bases into flow electrode solutions needs to be carefully optimized in terms of their concentration [74]. A proper amount of acid or base that maximizes the SAC should be added based on the degree of faradaic reaction with different types of flow electrodes.

One study investigated the effect of flow electrode recirculation in within-chamber (WC) mode (anodic and cathodic flow electrodes recirculated in respective chambers), or cross-chamber mode (anodic and cathodic flow electrodes recirculated across the chambers) on pH, faradaic reactions, and energy consumption [75]. The purpose of mitigating faradaic reactions in the FCDI process is in order to reduce energy consumption and prevent the oxidation of water and carbon in the electrode. Likewise, operations in the cross-chamber mode minimized and stabilized the pH gradient between anodic and cathodic flow electrodes (10.4 ± 0.08), and reduced the faradaic reaction, enabling stable operation of the FCDI unit.

3.3. FCDI cell operation

The design of the FCDI cell should give consideration to the types of flow electrodes and electrolytes. Research interest in designing FCDI cells has emerged since 2017, resulting in the development of several innovative operation modes, as illustrated in Fig. 5. The initially developed operational design was the open cycle (OC) operation mode (Fig. 5(a)), where an infinite number of flow electrodes was continuously supplied to the FCDI unit. This mode was reported to exhibit excellent desalination efficiency [62,76]. However, supplying an unlimited number of flow electrodes is not practical and expensive. Closed cycle (CC) operations use a fixed number of flow electrodes, considered a more practical and feasible FCDI mode.

There are two ways to enhance FCDI performance in CC mode: (1) designing electrode flow in an isolated closed cycle (ICC, Fig. 5(b)), [77] or in the short-circuited closed cycle (SCC, Fig. 5(c)) [45,76,78]; and (2) optimizing cell operational parameters including the amount of electrode, electrolyte concentration, and number of feed flow routes. Whilst conventional FCDI cells consist of two chambers for electrolytes to flow through and are separated by a space through which the feed water flows, the ICC and SCC modes are distinguished by the way the flow electrode is managed [11]. In the SCC mode, the cationic and anionic flow electrodes are collected together in a single reservoir outside the FCDI cell, after which electro-neutrality of the solution is achieved. This facilitates the desorption of cations and anions from the surface of flow electrodes. The isolated closed-cycle (ICC) mode operates in the same manner as the SCC mode during the adsorption stage, whilst the cationic and anodic flow electrodes are collected in separate reservoirs outside the FCDI cell.

Another recent study investigated the voltage-current (V—I) characteristics to optimize FCDI cell operation [79]. As the FCDI process is electro-based, a higher ion removal performance may be theoretically attained by simply applying higher voltages. The instability of the FCDI cell in over-limiting current regimes has restrained the realization of this theory. Through analysis, it was observed that when the FCDI process occurs under a linear V—I relationship, the performance of the unit was continuous and stable even during the over-limiting current regimes.

Process optimization of the FCDI unit has been validated through the modeling of key operational parameters. The results have been related to the energy consumption of the system using a novel equivalent film-electrode (EFE) model [80]. Based on the trade-off relationship between the ASAR and SEC, favorable operational conditions of the AC loading rate (w/v %) and feed concentration have been suggested through

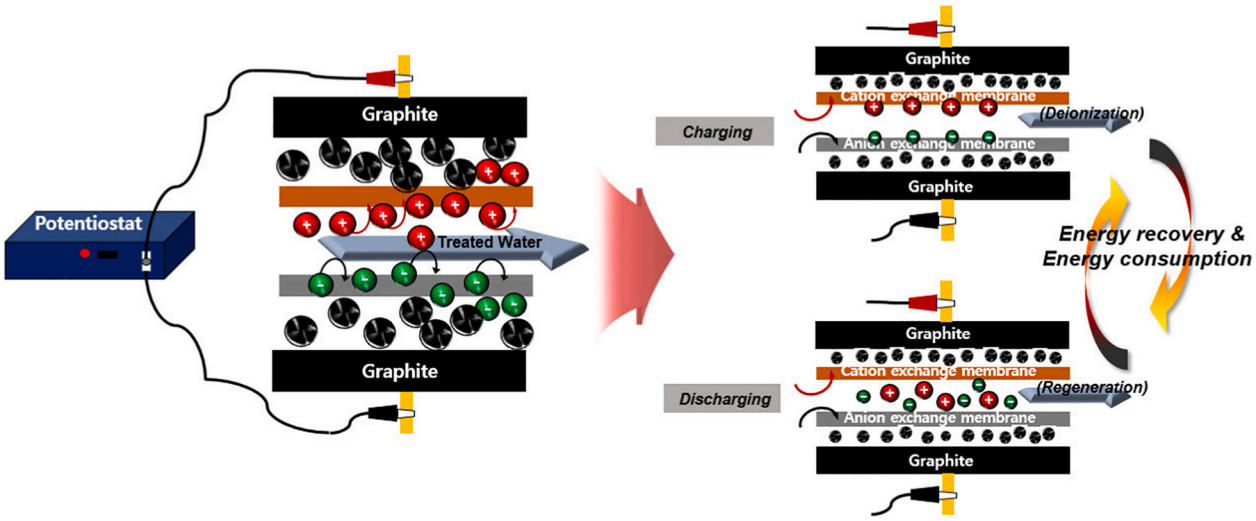

Fig. 6. Energy efficiency of flow-electrode capacitive deionization determined by charging and discharging, thus energy consumption and recovery.

simulation. Higher carbon content conditions (5%, 10%, and 15%) have demonstrated an increase in ASAR with a dramatic jump in SEC due to the increased viscosity of the flow electrode solution, which requires greater pumping energy. An increase in feed concentration (10, 17, and 30 mM), or reduction in effluent concentration has led to less favorable conditions for FCDI operation, apparent as a greater amount of ion content to be removed would require more energy.

Fouling is a key issue that greatly influences the long-term performance and stability of the FCDI process. Fouling occurs on the flow electrode and on the IEM. The CDI and MCDI processes adopt a stationary electrode that is able to serve as a platform for the build-up of an organic fouling layer. The fouling potential of the flow electrode is expected to be lower than the stationary electrode as flow dynamics are able to reduce the foulant attachment on the surface of the suspended particles [81]. An ion exchange membrane placed between the flow electrode and feed water acts as a barrier preventing foulants from entering the flow electrode solutions [82,83].

Cleaning strategies investigated for stationary carbon electrodes in CDI may be adopted for flow electrode washing. Studies have examined electrode washing in MCDI with acid/alkaline solutions following the treatment of wastewater effluent using biological treatment processes, groundwater, and synthetic solutions containing model organic foulants (i.e., humic and alginic acids) [83–86]. The results have shown that the alkaline solution successfully removed organic fouling to recover a salt adsorption rate up to 80–90% of initial performance. Another study reported conflicting results showing that the alkaline washing solution degraded the polyvinylidene fluoride (PVDF) binder, which had prompted the loss of carbon electrodes. This led to a decrease in the SRE of MCDI [83]. The same issue was not an obstacle for the FCDI system, as it uses suspended particles within a liquid solution as an electrode.

The FCDI process may have challenges associated with fouling of the IEM. A recent study using sodium alginate and humic acid as model foulants reported the deterioration in performance from FCDI as a result of IEM fouling was not significant. The authors attributed this to the initially low adsorptive tendency of organic foulants on the IEM surface and the subsequent spontaneous detachment of organic foulants from the surface in the discharging step due to the applied reverse charge [83]. In the presence of $CaCl_2$, a strong binding between sodium alginate and calcium ions formed a dense “egg-box shaped” alginate gel layer, this compromised the salt adsorption efficiency [83,87]. The impact of IEM fouling on FCDI performance has also been investigated over the long term (15 d) with feed solutions containing sodium alginate and humic acid foulants. Evident surface coverage of the IEM by these foulants was observed, subsequently reducing the salt adsorption efficiency [88].

4. Improving energy efficiency

Energy efficiency is a prime factor that requires critical assessment for industrial applications of FCDI technology. Despite its importance, only a fraction of existing research papers deal with energy consumption. There are two main aspects governing the energy efficiency of the FCDI process, illustrated in Figs. 5 and 6: (i) types of flow electrode operation (i.e., ICC, SCC, and OC); and (ii) operating modes of the adsorption and desorption steps (i.e., constant voltage and constant current).

4.1. Energy efficiency

The majority of studies reported that FCDI requires additional energy compared to MCDI to overcome the charge transfer resistance between the flow electrode and current collector. However, FCDI with potentially higher water recovery may have a lower SEC than MCDI as SEC is calculated based on the volume of the product water [45,60,89].

A typical FCDI unit consists of two separate electrode cells for adsorption and desorption steps; as such, ideally 100% water recovery is possible. At present, in-depth studies that evaluate the energy efficiency of FCDI based on water recovery are currently lacking. One modeling study reported FCDI energy consumption to depend on the carbon weight percent of flow electrodes in the electrolyte [60]. Another study reported that energy consumed during the adsorption step may be recovered by up to 36% during the desorption phase [90].

The effect of carbon mass loading on FCDI energy consumption has also been investigated under a constant current mode. It is known that voltage is inversely related to the impedance/resistance of flow electrodes, as defined by Ohms Law. The impedance of a flow electrode increases under lower mass loading conditions, as the lower carbon content makes it difficult for charge transfer between electrode particles due to the loss of contact points. Likewise, an increase in carbon mass loading from 5 to 23 wt% was reported to have decreased the deionization energy requirement from 92 to 28 J, achieving approximately 18% salt removal [44,60].

Another critical point is the pump energy required to circulate flow electrodes, which is not required for CDI and MCDI with stationary carbon electrodes. Although there is awareness in the research field of this extra energy demand for flow electrode pumping, there are few studies that have investigated the details. Pumping energy consumption has been demonstrated to be significant in FCDI systems; as such, FCDI

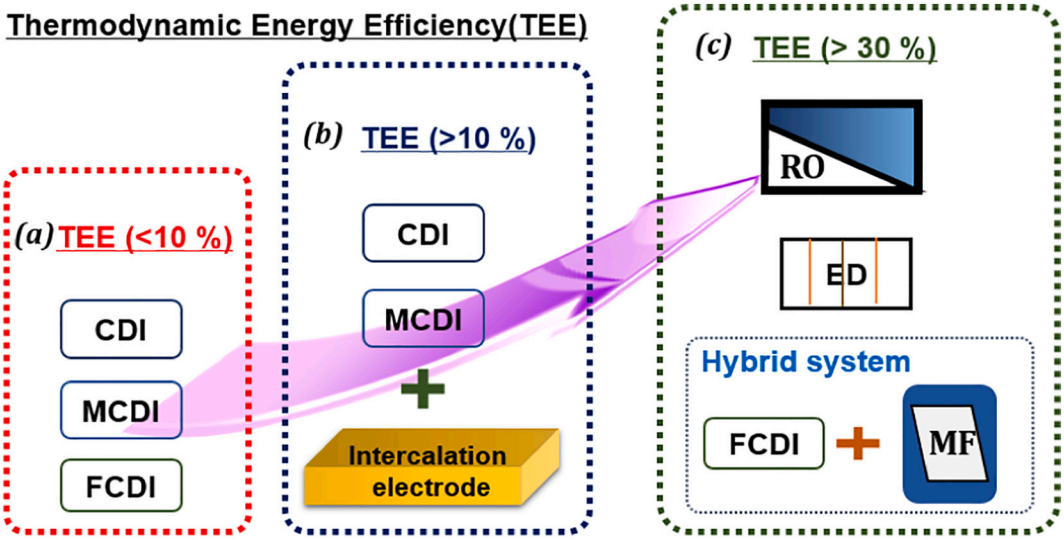

Fig. 7. Comparison of the thermodynamic energy efficiency (TEE) of electrochemical-based desalination approaches [97]: (a) CDI, MCDI, and FCDI with carbon electrode materials (red box), (b) CDI, MCDI with intercalation electrodes (blue box), and (c) RO, ED, and FCDI–MF Hybrid system (green box). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

operation requires optimization in terms of its low flow rate, high carbon content, and intermittent flow cell operation [20,44,91]. The current efficiencies range between 60% and 80%, consistent with previous results. Further improvements to efficiency may be achieved by decreasing the operating current density or feed solution concentration.

4.2. Improvements for energy saving

The FCDI system is able to reduce energy using various process modes (i.e., ICC and SCC), the key difference between these modes being the electrical energy. For the ICC mode, it is difficult to release the adsorbed Ca^{2+} during the desorption stage (i.e., flow-electrode regeneration step) even with reverse voltage. The inability to desorb Ca^{2+} may partly explain the extremely low energy recovery with the hardness in the influent. Several strategies have been proposed to mitigate the effect of hardness on effective CDI desalting, as the presence of divalent cations (i.e., Ca^{2+}) may severely impede energy recovery. One such method is the modification of carbon particle surfaces by calcium alginate coating. During the SCC mode, the flow-electrodes do not require electrically driven regeneration with ion accumulation in carbon suspensions potentially managed by cost-effective physical means. The discharging of flow-electrodes under 0 V in ICC mode did not guarantee the complete release of adsorbed ions with any additional discharging step in reverse voltage leading to extra energy consumption. As such, the SCC mode consumed only 20–50% of energy used in ICC configuration whilst achieving similar efficiency.

The operational modes of the adsorption/desorption steps, constant voltage (CV) and constant current, are also critical in evaluating the energy consumption of the FCDI process. By definition, these two modes are means of supplying power to the FCDI system. In CV mode, a constant voltage is applied to the unit, whilst a constant current is introduced for the constant current mode. In both cases, a higher working voltage under CV mode naturally results in improved process performance and higher energy consumption, whilst a higher current density under the constant current mode generates equal results. However, the predominance of the CV operation mode in recent FCDI research has occurred for several reasons; making it challenging to undertake a clear comparative analysis of these two operational modes in terms of performance and energy consumption. The first reason is that direct observation of salt adsorption rate is possible by controlling the applied voltage, which allows for intuitive investigation of process performance. Second, the aim of FCDI is the electrosorption of ions through non-faradaic reactions, and since water electrolysis occurs in the voltage range of >1.23 V, the applied voltage of the system needs to be stably controlled to within the non-faradaic window (<1.2 V).

Despite the higher energy consumption for desalination and the pumping energy required for electrolyte and feed solution circulation, FCDI has advantages in terms of its continuous desalination with great removal efficiency and its ability to treat high TDS concentration solutions as flow electrodes are repeatedly regenerated through desorption. Following continuous desalting, there is constant energy recovery during the FCDI process, resulting in higher energy efficiency. As such, the majority of FCDI studies that address the energy aspect primarily focus on energy recovery.

Several factors influence operational efficiency in the FCDI process, the first of which is charge percolation. Charge percolation within the electrolyte is limited by dynamic particle–particle interactions as opposed to established solid-stage conduction pathways [14]. Thus, the flow rates of the feed solution and electrolyte crucially influence the kinetics and efficiency of the FCDI system.

Another influential parameter is power output. With the exception of the initial phase of operation when cell voltage steadily rises to set levels, stable power density was observed for all systems. This is contrary to conventional capacitive systems, which require fixed carbon electrodes where water streams are switched alternately, to recover the initial salt adsorption capacity of electrodes [92,93]. Such intermittent operations render disadvantages as it delivers a non-constant power output. With flow electrodes, power output is constant in time, suggesting that continuous flow electrode systems may be a more competitive option. As such, there have been proposals for continuous energy generation through capacitive mixing technology using the difference between gaseous CO_2 concentration and water salinity [44].

In particular, systems based on salinity gradients have a lower open-circuit voltage when MEA (mono-ethanolamine) is added to solution compared to pure water. This also has low resistance and up to 10 times the power density. This technology may realize CO_2 generated when using fossil fuels as an energy source and contribute to the energy strategy. One critical difference in energy recovery is ionic diffusion between electrolytes and the feed solution through IEMs [89]. When deionized water was used as the feed solution, energy recovery was dependent on the charged voltage, explained by the energy loss during the charging/discharging step. Regardless of the applied voltage in the

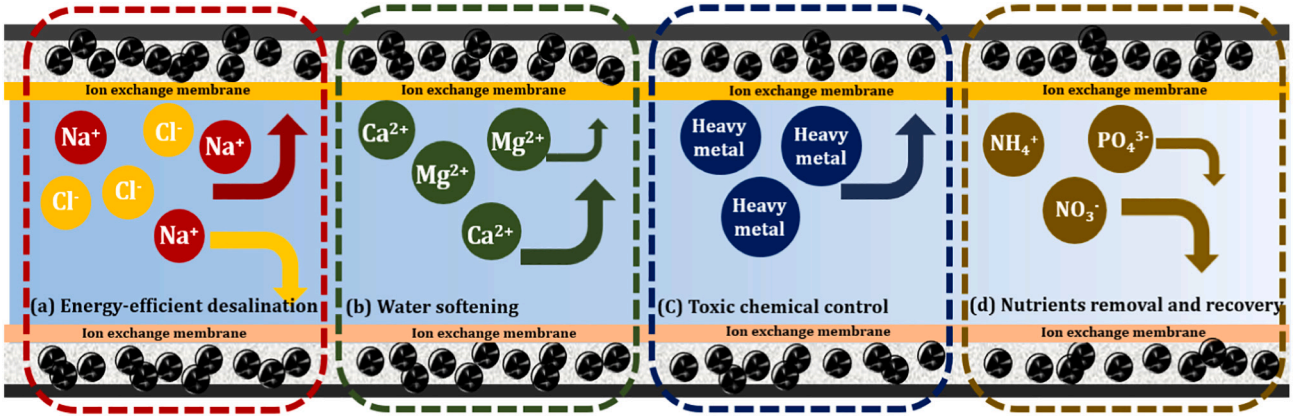

Fig. 8. Potential applications of FCDI technology in (a) energy-efficient desalination; (b) selective water softening; (c) removal of toxic chemicals; and (d) recovery of nutrients.

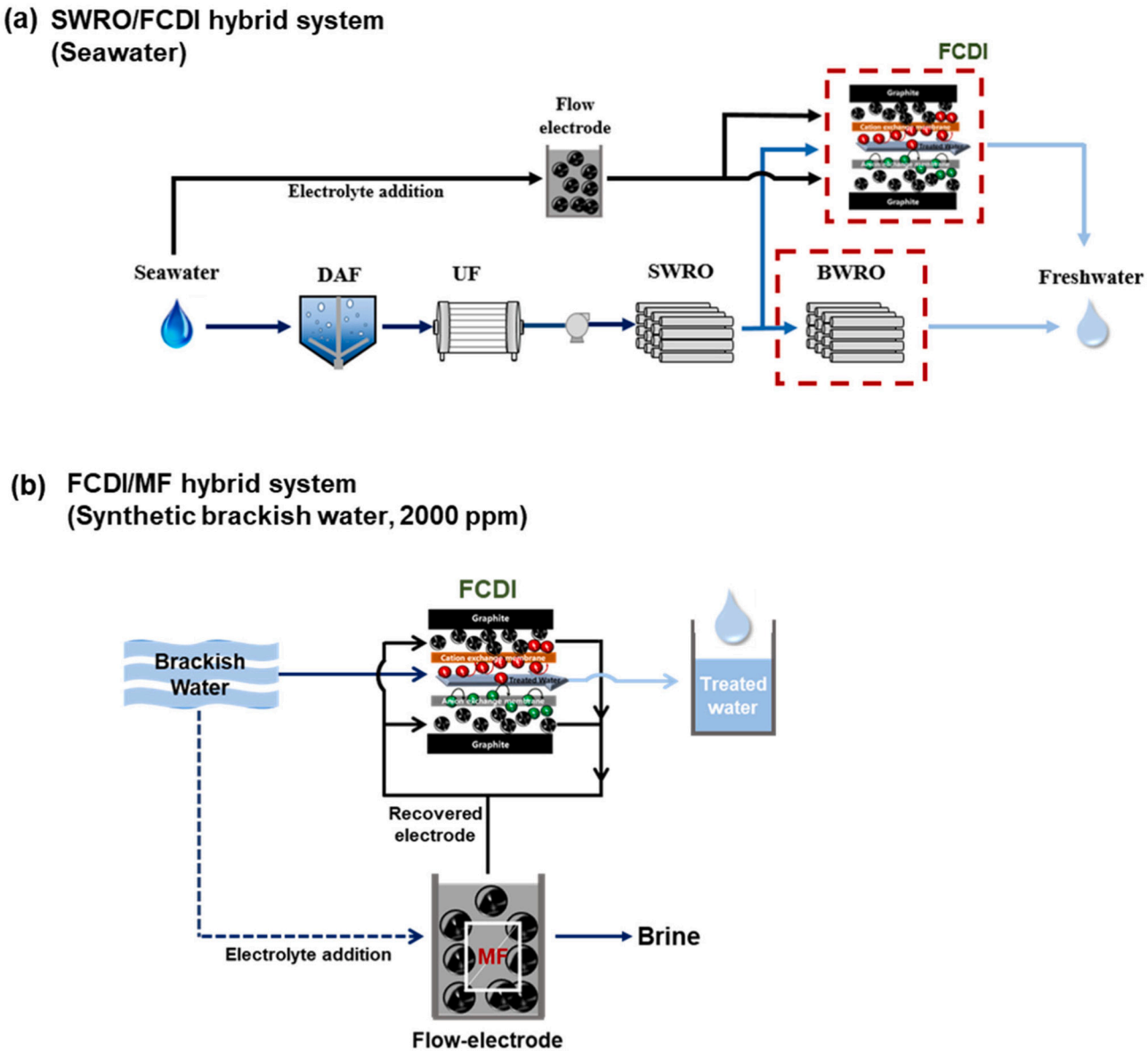

Fig. 9. Flow diagram of the conceptual (a) SWRO-FCDI; and (b) FCDI-MF hybrid processes for enhanced desalination efficiency.

adsorption phase, a relatively constant energy recovery of ~20% was achieved when saltwater was introduced during the energy recovery phase. This was explained by the difference in the ion concentration between saltwater and the electrolyte of the flow-electrode. This means that a higher TDS concentration of the feed solution compared to the electrolyte may be beneficial for removal efficiency. Additionally, the supplied energy may be less recoverable due to the disturbed overall ionic charge flow [89]. For energy-efficient flow capacitive deionization to be fully realized, there is a need for comprehensive scale-up studies that focus on continuous flow and plug flow operational modes.

4.3. Quantification of energy efficiency

To quantify the energy efficiency of FCDI, previous studies have presented the ratio of Gibbs free energy (ΔG) to electrical energy consumption, known as thermodynamic energy efficiency (TEE), as shown in Eq. (3) [81,91,94,95]:

$$\mathrm{TEE} = \frac{\Delta G}{SEC_{electric}} \tag{3}$$

Such analyses are questionable as pumping energy has not been taken into consideration. It was also observed that higher ion removal performance and water recovery required a larger ΔG. Conventional CDI and MCDI processes generally showed ΔG values <0.01 kWh/m^3 because of lower desalination performance and water recovery, whilst the FCDI process had a slightly higher ΔG value of 0.05 kWh/m^3. With regard to TEE, the majority of the CDI, MCDI, and FCDI-based carbon electrodes had TEE values <10% on average, as shown in Fig. 7. One study utilizing an FCDI-MF hybrid system reported a TEE value of ~30%, comparable to those of RO and electrodialysis processes operated under similar conditions (i.e., low/medium feed water salinity and high water recovery) [10,45,60,41,70,96].

Chung et al. [81] also demonstrated the quantitative energy consumption through the SWRO-FCDI hybrid system using natural seawater. This system could easily be integrated into an existing SWRO plant. The SEC of the hybrid system increased in the applied voltage range (0–0.25 V), where it was less than 0.005 kWh/m^3, and increased to 0.03 kWh/m^3 at 0.50 V. These results suggest that energy consumption of the FCDI system was lower than that of the typical brackish water desalination (BWRO) process. Thus, the proposed SWRO-FCDI hybrid system offers a promising solution to realize low-energy desalination systems by eliminating second pass BWRO in typical SWRO desalination plants.

4.4. Analysis of energy/economic feasibility

Assessing the economic feasibility of the FCDI process based on energy efficiency analysis is critical in terms of its implementation. As FCDI is still at an early research development stage, there is very little literature offering comprehensive techno-economic analyses. One study evaluated the energy consumption of FCDI used for post-treatment of the SWRO process in replacement of the BWRO unit. To treat the permeate from the first-stage SWRO unit (salinity of ~550 mg/L), FCDI was analyzed to consume 0.03 and 0.09 kWh/m^3 to reduce salinity to 300 and 150 mg/L, respectively, in a short 30 min operation [81]. An extended FCDI operation for 120 h further reduced permeate salinity to 12 mg/L; this is even better permeate quality than that produced from typical BWRO systems [98], with ≈0.3 kWh/m^3 energy consumption. As the BWRO energy consumption is typically in the range of 0.2–0.4 kWh/m^3, the ≈0.3 kWh/m^3 of energy consumption under the operating conditions demonstrates the economic feasibility of the FCDI process [1,81,99].

Another simulation study compared the energy consumption of the CDI, MCDI, and FCDI processes based on the same permeate salt concentration. Data were evaluated using TEE and eight common parameters including feed water concentration, electrode flow rate and charge. The simulations reported an energy consumption normalized to salt removal (ENAS, μmol/J) of 0.63–12.8, 9.84–16.1, and 8.69–14.3 for CDI, MCDI, and FCDI, respectively. In terms of volumetric energy consumption, CDI, MCDI and FCDI required 0.64, 0.31 and 0.42 kWh/m^3, respectively [22]. These results are comparable to that of those reported for pilot and full-scale BWRO systems (0.5–7.7 kWh/m^3) [1,100], highlighting the economic viability of the FCDI process.

5. Potential FCDI applications

Recent reviews have reported a wide spectrum of MCDI applications including brackish water desalination, water softening, and selective removal of contaminants such as heavy metals, phosphates, and nitrates (Fig. 8) [13]. As FCDI and MCDI share identical electro-driven desalination principles, it is envisioned that FCDI will have a similar application potential. Process hybridization with existing desalination technologies is a promising strategy to expand the range of possible FCDI applications (Fig. 9). For instance, FCDI integrated with RO or microfiltration (MF) has the potential to achieve higher SREs, producing an improved quality of freshwater [81,91]. Examples of these integrations are discussed in detail in the following subsections.

5.1. Energy-efficient desalination

FCDI has the potential to become an energy-efficient alternative to existing seawater and brackish water desalination technologies. The use of conductive flow electrodes enables high ion adsorption capacity with low flow viscosity, facilitating effective electron charge transport by preventing agglomeration of flow electrodes. It also promotes desalination performance by modifying the asymmetric structure of the electrode and modification of the electrolyte.

Integration of FCDI with existing desalination processes may further improve desalination efficiency. An FCDI-NF hybrid system was suggested to treat feed water with a relatively high TDS concentration of ~10,000 mg/L at 70% water recovery. This system showed good desalination performance, producing permeate water quality that satisfied drinking water standards (TDS <500 mg/L). Energy consumption of the hybrid system was also assessed to be 16–20% lower compared to a stand-alone BWRO system. Further rigorous energy analysis is required to confirm this conclusion, whereby the two systems are compared at equivalent scales and under similar operating conditions (i.e., feed water salinity, rejection rate, and water recovery) [95].

Recent studies have also investigated other hybrid FCDI processes; Fig. 9(a) shows the combined SWRO-FCDI process [81]. The hybrid SWRO-FCDI process demonstrates similar freshwater production performance as conventional SWRO-BWRO processes. However, in the current two-pass SWRO system composed of a SWRO-BWRO pair, a remineralization process is required to supplement depleted divalent cations such as Ca^{2+} to prevent pipe corrosion in water distribution. In contrast, the SWRO-FCDI system is able to remove monovalent and divalent ions at differing removal efficiencies using a selective IEM. This reduces the operating cost by eliminating such post-treatment steps. This hybrid process is further optimized for desalination as the FCDI stage may be operated without the additional injection of electrolytes and using salts in seawater as the electrolyte [81].

Fig. 9(b) illustrates a system combining FCDI with MF operated in the SCC mode using brackish water as the feed solution [91]. This conceptual process operated through four main steps: (i) salt ion adsorption by flow electrodes across the IEM; (ii) flow electrode charge neutralization/regeneration in an external tank containing a submerged MF module; (iii) ejection of brine (water and salt ions within the flow electrode solution) via the submerged MF module; and (iv) addition of feed solution into the flow electrode solution to maintain volume and electrolyte concentration. The FCDI-MF hybrid process is energy-efficient compared to other methods of flow electrode regeneration through continuous operation.

5.2. Water softening

FCDI demonstrates great promise for water softening. A recent study demonstrated the FCDI treatment of a feed solution containing 2000 mg/L of NaCl and 150 mg/L of $CaCl_2$, resulting in a product water of <500 mg/L of TDS and <15 mg/L of $CaCl_2$, with an SEC of ~0.44 kWh/m^3 [45]. Although the study did not account for the energy consumption for electrode and feed-flow pumping, the reported SEC value was similar or lower than 0.4–0.5 kWh/m^3; this is typically required by current BWRO desalination systems. Another study introduced a nanofiltration (NF) membrane (NF270, Dow Filmtec.), instead of the typical IEMs in FCDI to improve selectivity for divalent ions (i.e., Mg^{2+} and SO_4^{2-}) over monovalent ions (i.e., Na^+ and Cl^-) [94]. When substituting the NF membrane with the anionic exchange membrane (i.e., NF-AEM-FCDI), a much higher current efficiency (53–94%) was observed compared to the NF-CEM-FCDI (27–58%) due to the negative surface charge of the NF membrane [94].

Although these studies have demonstrated the high potential of FCDI for water softening, there continues to be practical challenge associated with a limited ion removal rate of <27%. One approach to further improve softening efficiency includes FCDI operation in SCC mode (Fig. 5(c)). In this mode, flow electrodes are mixed and regenerated by charge neutralization in an external reservoir, aiding in the inhibition of scale formation on the surface of electrodes [41,62]. Additionally, SCC operation has been observed to critically inhibit the acquisition of charge by the competition between electron acceptors and donors [45]. In contrast to SCC mode, desorption of Ca^{2+} ions from flow electrodes was limited in ICC mode even with the application of a reverse current. The low desorption rate was because the pH of the cathodic flow electrode solution increased dramatically during the charging/adsorption step. This generated calcium scales on the surface of AC particles and there was a lack of free Ca^{2+} ions in solution. To tackle the limited desorption efficiency in ICC mode, AC flow electrodes coated with calcium alginate have been developed and have demonstrated improved FCDI water softening performance.

5.3. Toxic chemical control

Toxic heavy metals such as lead, cadmium, copper, and chromium in water and wastewater are of critical environmental concern [15,101,102]. Electrochemical and membrane-based water treatment processes and chemical precipitation and adsorption, have been used to remove heavy metals [96,103,104]. However, these conventional approaches suffer from operational problems associated with secondary by-products and intensive energy consumption [105]. A recent investigation showed high removal of copper with CDI and FCDI [106]. Another study demonstrated the effective removal of uranium with FCDI in SCC and ICC modes, decreasing the uranium concentration from 40 to <10 μg/L (i.e., >75% removal efficiency) [107]. The removal of lead was evaluated using the CDI process, and the pH of the solution was found to play a major role in influencing removal rate [108]. As FCDI performance is less sensitive to the pH of the feed solution, it is expected that there is a higher removal efficiency of lead and other heavy metals that speciate depending on pH in FCDI compared to CDI.

5.4. Nutrient removal and recovery

The removal and recovery of ammonia and phosphorus that cause eutrophication in natural aquatic ecosystems are possible niche applications of FCDI [109–111]. Conventional IEMs and pressure-driven membrane processes were examined for the pre-concentration of ammonia in municipal wastewater; however, several challenges continue to restrict their practical application.

FCDI technology allows the chemical-free recovery of ammonia from wastewater, and has been tested to recover ammoniacal nitrogen from low-strength municipal wastewater. Under optimized FCDI operating conditions of applied voltage, flow rate, conductive additive, pH, and initial feed solution concentration, the effective ammonia concentration increased by 20-fold to reach an NH_3-N concentration of 322 mg/L. This demonstrates that FCDI is a promising alternative for ammonia recovery, particularly for wide ranging initial ammonia concentrations in feed water [112].

Another study proposed an FCDI process integrated with a hydrophobic hollow fiber membrane contactor, termed “CapAmm” for ammonia recovery [113]. In this process, ammonia migrated across a cation exchange membrane and accumulated in the cathode chamber of the flow electrode. Then, ammonia turned into a dissolved form of $NH_{3(aq)}$, stripped by a membrane contactor in $NH_{3(g)}$, and finally recovered as ammonium sulfate ($(NH_4)_2SO_4$). Approximately 9.9–21.1 kWh per kg of N production was required for ~90% and ~60% ammonia removal and recovery rates, respectively. This is comparable to those of other electrochemical-based ammonia recovery systems such as a hydrogen gas recycling electrochemical cell, a gas permeable membrane contactor, and an electrochemical cell combined with air stripping [114,115]. Thin film composite membranes that produce higher current efficiency may be utilized to enhance the ammonia removal rate [116].

The recovery of ammonia through process design has also been investigated in a study that utilized a novel stacked FCDI cell [117]. This study used potassium sulfate (K_2SO_4) as an additive, where the FCDI process with the use of a monovalent cation-selective exchange membrane (M-CEM) yielded a product purity increase from 50% to 80%, and an ammonia recovery rate two times that of the standard cation exchange membrane (S-CEM). The performance improvement was attributed to differences in the physicochemical properties (i.e., functional groups of ion-selective membrane surface, zeta potential, water contact angle, and electric resistance) of the two membranes.

Several studies have investigated the removal and recovery of phosphorus from wastewater by FCDI. Specifically, with an initial phosphorus concentration of 10 mg/L, the AC content of 10 wt%, feed water pH of 5.0, and an applied voltage of 0–1.2 V, a phosphorus removal as high as 97% was demonstrated. This highlights the FCDI potential to recover valuable nutrients from wastewater [118]. Phosphorus recovery in the form of H_3PO_4 was also recovered in a study from phosphoric acid industry wastewater containing high concentrations of fluoride and phosphate ions; this was accomplished by using a two-step process involving a silica reactor and FCDI. In the initial step, fluoride ions were removed via the silica reactor, whilst the pH of the solution was lowered concurrently. The effluent of the silica reactor, currently at a pH of ~1.0, allows H_3PO_4 to exist as the dominant species of the phosphate system. Treatment of the solution through the FCDI process removed all other ions, whilst the uncharged H_3PO_4 was collected in the permeate at a ~90% recovery rate [119]. Another study also evaluated the removal efficiency of phosphate through pH variation of feed and electrolyte solutions. The results showed that a 90% increase in removal efficiency was observed at pH 5.0, compared to a pH 9.0 of the feed solution. A different trend was observed for the electrolyte solution in which phosphate removal was ~74.8% higher at pH 11.0 than at pH 5.0. These results were associated with changes in the surface charge of the AC under differing pH values, altering the adsorption efficiency [120].

6. Future direction for improving feasibility and applicability of FCDI

FCDI technology has demonstrated continuous desalination performance using flow electrodes and an electrode regeneration system. This novel desalination approach operating under low electric potential (typically <1.2 V), and without hydraulic pressure is expected to provide energy-efficient desalination over conventional electrochemical and membrane-based desalination technologies. Further research on process optimization, including the enhancement of the flow electrode performance is required to enhance the feasibility and expand the applicability of FCDI. For instance, although AC materials have been the

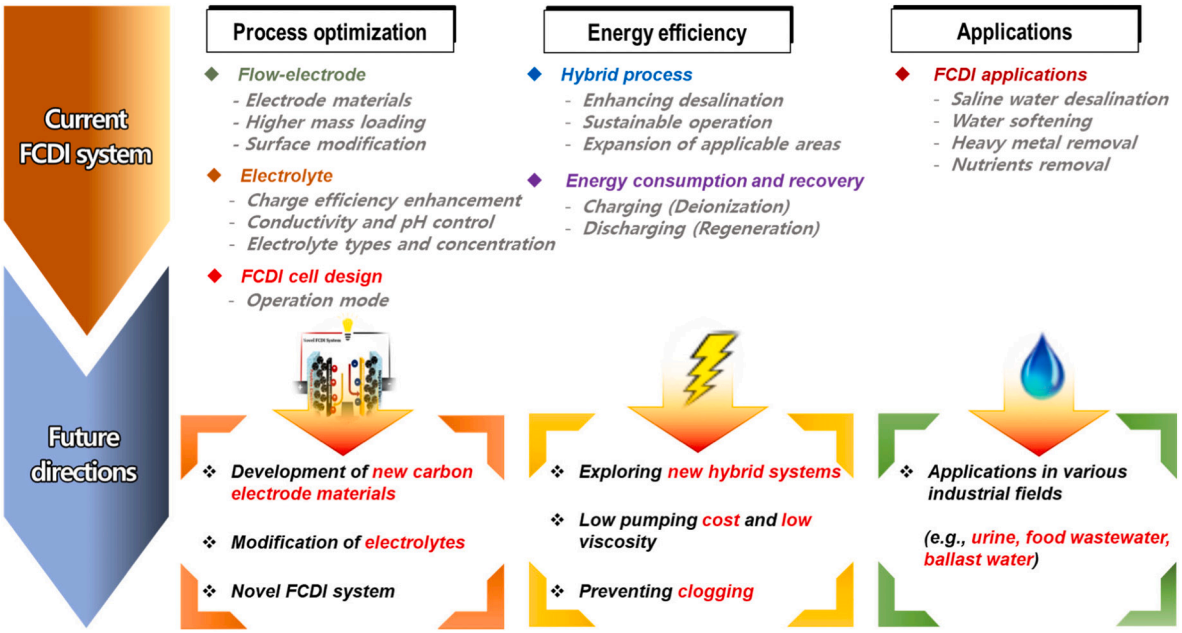

Fig. 10. Summary of FCDI system; current and future directions.

main focus of investigation and development for use as electrodes, other innovative platforms such as catalytic micro-particles may improve FCDI desalination performance. Hybrid processes that reduce electric energy demand and maximize removal efficiency may be realized by integrating FCDI with existing membrane-based processes (i.e., SWRO, BWRO, NF, and MF). Fig. 10 shows the potential applications of FCDI in water and industrial wastewater treatment and resource recovery.

6.1. Process optimization

This paper has discussed the importance of flow electrode materials, electrolyte selection and concentration, flow cell design, and various operating conditions that influence the performance of FCDI. More specifically, high loading of flow electrodes, suppression of redox reactions at the electrode surface, improvement of material-specific properties, and optimized charge transport and electric resistance of the electrolyte are critical for the desired FCDI performance. Many of these aspects have been investigated under limited FCDI operation modes (i.e., ICC, SCC, or OC mode). As such, the direction of FCDI process optimization should focus on developing new catalysts, the modification of electrolytes, and novel FCDI operations.

6.2. Improving energy efficiency

To properly discuss the energy efficiency of FCDI, understanding the mechanisms underpinning the process is crucial. The system operates by applying potential to the unit, contributing to energy recovery during the charging step (i.e., freshwater production). In contrast, energy is consumed whilst flow electrodes are regenerated during the discharging step. To date, there has been a lack of a detailed systematic energy analysis and in addition, sequential combinations (i.e., hybrid systems) need to be examined to enhance freshwater production efficiency whilst saving energy compared to existing commercialized processes. The commonly neglected pumping energy should also be evaluated in future studies to sufficiently reflect realistic FCDI process conditions. Lastly, the development of techniques that can effectively minimize the clogging of carbon-based flow electrodes with low viscosity is required to maximize process performance whilst maintaining the energy efficiency of the FCDI system.

6.3. Evaluation of process applicability

Currently, there is an absence of comprehensive technical reviews on the applicability of the FCDI process, as previous studies have largely focused on desalination with brackish water as the feed. The industrial expansion of the FCDI process requires further research in view of desalination performance and energy recovery through using different types of feed waters and/or under diverse applications (i.e., softening, heavy metal control, and nutrient recovery). It is also important to attempt to scale up the process to satisfy real water treatment conditions. Nevertheless, securing freshwater using ion adsorption technology through selective membranes and flow electrodes is the highest priority. Thus, the first challenge for FCDI is the application of differing feed waters to examine process applicability. In addition, as the FCDI process is electrochemical-based, there are also challenges associated with treating various wastewaters (i.e., urine, food wastewater, and desulfurized wastewater) that contain multiple types of ions (i.e., NH_4^+, Cl^-, SO_4^{2-}). This is heavily dependent on the nature of the wastewater; as such, accommodating for this diversity in feed water ion composition and concentration needs to be addressed for the widespread application of FCDI technology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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