

# 新竹科學工業園區管理局





# 低耗能水再生技術-電容脫鹽及相關案例介紹

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#### Outline: 電容脫鹽技術







#### 水資源與能源之交互關係

## 聯合國:全球對能源的飢渴威脅水資源

#### thirsty energy

energy and water's interdependence energy needs water Energy production

processes require water

- hydropower
- thermoelectric cooling
- power plant operations
- fuel extraction and refining
- fuel production

#### water needs energy

Water production, processing, distribution, and end-use require energy

extraction

- treatment
- transportation



WORLD BANK GROUP www.worldbank.org/thirstyenergy



#### 水資源與能源關係之思維



# 氣候變遷對臺灣水資源之影響

- Intergovernmental Panel on Climate Change (IPCC) Climate Change Assessment Report
  - Precipitation extremes
  - Increase in intense and heavy episodic rainfall events
  - Longer relatively dry periods





**IPCC AR5, 2013** 

臺灣氣候變遷科學報告 2011

中華民間100年11日



# 新興水資源之開發與推動(水利署)



水資源多元化

新興水資源:海水淡化



#### 新興水資源:再生水在水循環扮演之角色



http://www.water.ca.gov/recycling/

# 低耗能脫鹽技術與現有污水處理場結合



#### 脫鹽技術的發展與演變





**Reverse Osmosis** 



Schematic diagram of major desalination technologies and their relative contributions to worldwide installed capacity for seawater and brackish water desalination.

#### 新穎(低耗能)脫鹽技術之現況分析

處理程序	正渗透(FO)	電去離子(EDI)	電容去離子(CDI)	薄膜蒸餾(MD)
技術原理 與 關鍵技術	利用選擇性半透膜兩邊 溶液其溶質濃度差異所 造成的滲透壓差做為 動力,水分子自發地從 低溶質濃度的過程 質濃度的過程	結合IEM以IER的複合 型分離技術。EDI利用 IEM對陰、陽離子的選 擇性,以及IER的離子 交換作用,在直流電場 操作下進行離子分離程 序	藉高比表面積及導電性之時電荷吸荷都電行。 一個一個一個 一個 一個 一個 一個 一個 一個 一個 一個	利用疏水性薄膜兩側水溫高 低溫差,以薄膜兩側流體接 觸面的蒸氣壓差為趨動力, 將水蒸氣分子經薄膜孔洞, 由高溫側傳輸到低溫側後凝 結成液體,而達到分離水分 子之目的。
目標 污染物	各類水溶性溶質	重金屬、 溶解性無機鹽	重金屬、帶電離子、 溶解性無機鹽	揮發性溶劑中離子、 巨分子、膠體、 以及非揮發性物質
技術特點	<mark>自發性驅動</mark> 高離子排除率、 不易發生積垢問題	改善傳統 電透析(ED)程序 增加對弱解離性物種 處理效果	<b>不需使用薄膜</b> (無積垢) 低電壓操作、 可由綠能驅動運行	<mark>熱能可由廢熱驅動</mark> 較傳統蒸餾程序有低能量與 空間需求、高離子排除率
關鍵技術	薄膜製造技術 & 提取液開發	薄膜製造技術 & 陰陽IER混合比例	碳電極材料製造技術 & 模組設計	薄膜製造技術 & 模組設計
主要應用	<ul> <li>▶高營養鹽污泥</li> <li>▶濃縮脫水</li> <li>▶有機污染物去除</li> <li>▶二級放流水的處理</li> </ul>	<ul><li>&gt;純水的製造</li><li>&gt;重金屬離子的去除</li></ul>	<ul> <li>&gt;海水淡化</li> <li>&gt;硬水軟化</li> <li>&gt;地下水整治</li> <li>&gt;重金屬離子去除</li> </ul>	<ul> <li>▶海水淡化</li> <li>▶非揮發性物質移除</li> <li>▶揮發性有機物質移除</li> <li>▶酸液濃縮</li> </ul>
重要 参考文獻	(Holloway et al., 2007) (Zhang et al., 2013) (Zhang et al., 2012)	(Arar et al., 2014) (Strathmann, 2010) (Dermentzis et al., 2009)	(Farmer,1997) (Xu et al., 2008) (Seo et al., 2010)	(Lawson and Lloyd, 1997) (Khayet et al., 2003) (Zhang et al., 2015)

#### 電容去離子技術 (Capacitive Deionization, CDI)

#### ↓ 技術原理

- 以電荷分離與超級電容器工作原理,從水體中移除離子。
- 基於奈米孔洞碳電極,施加低電壓(~1.2 V)產生正極和負極,使 得水體中的陽離子、陰離子被庫倫作用力影響,電吸附於具相 反電性的電極中,進而在孔洞中發展電雙層。



電容去離子技術的工作原理

#### •研發動機

- 電容去離子技術被OCED 評估為未來最具發展潛力 的脫鹽技術。
- 低耗能、綠色分離的技術,
   可有效的去除水中的無機
   性離子,降低水體的導電
   度及總溶解固體濃度。

# 薄膜電容去離子技術 (Membrane Capacitive Deionization, MCDI)





Removal efficiency Energy efficiency

# 電容脫鹽技術的低耗能優點

#### Energy Considerations in CDI



CDI could be competitive technology at NaCl concentrations below 5000 mg/L. (M. M. Anderson et al., 2010)

- (Adapted from Oren et al., 2008)
- \*Energy consumption (2000 mg/L salty water):
  - RO:  $2.25 \text{ kWh/m}^3$
  - EDR:  $2.03 \text{ kWh/m}^3$
  - CDI:  $0.59 \text{ kWh/m}^3$ 
    - (Welgemoed and Schutte, 2005)

#### 電容去離子技術的特點

#### ↓ 主要特點

- 低壓操作
- 低電壓、低耗能
- 通道式流道,不易堵塞
- 產水率高(>75%)
- 無二次汙染 操作與維護簡便

#### ➡應用範圍

- 半鹽水淡化
- 飲用水淨化
- 家庭/工業再生水脫鹽
- 微量污染物的去除
- 重金屬的去除

脫鹽技術	技術原理
逆滲透 (RO)	<ul> <li>□外加壓力與反滲透膜</li> <li>□高壓下運行</li> <li>□薄膜積垢與操作維護複雜</li> <li>□能耗: 2.3~5.7 kWh/m<sup>3</sup></li> </ul>
電透析 (ED)	□電驅動與陰陽離子交換膜 □薄膜極化與水解現象 □消耗化學藥品
電容去離 子 (CDI)	<ul> <li>■電吸附與超級電容原理</li> <li>■通道式結構</li> <li>■OECD(2009)評估最具有 取代現有脫鹽技術之潛力</li> <li>■低耗能 0.5~1.0 kWh/m<sup>3</sup></li> </ul>

電容脫鹽技術的主要特點



#### 電容去離子技術之原理



#### 電雙層(Electrical Double Layer)的形成

- A charged surface in an aqueous environment leads to a potential difference across the solid/electrolyte interface.
  - ✓ Neutralization of space charge: counterion accumulation
  - ✓ Electrical double layer (EDL) formation
  - Electrosorption of ions



EDL is a very important interfacial phenomenon to many physical, chemical, and biological systems.



#### Historical development

#### ✓ Helmholtz:

A single-adsorption layer of ions with charge opposite to that of the surface

#### ✓ Gouy and Chapman:

A diffuse model of EDL, in which the potential decreases exponentially due to accumulation of counterions from the solution

#### ✓ Stern:

Combination of the Helmholtz singleadsorption layer and Gouy-Chapman diffuse layer models





Hydrated coion

Hydrated counterion



## 電雙層電容器/超級電容器 (Electrical Double Layer Supercapacitor)

Energy storage by formation of double layer when a voltage is applied to an carbon electrode immersed in an electrolyte



# 超級電容器的時代

# Where Do Batteries End and Supercapacitors Begin? Simon et al. (2014), *Science*











The mechanisms of capacitive energy storage

Electrochemical measurements can distinguish between different types of energy storage materials and their underlying mechanisms.

# 電容脫鹽技術的工作原理

#### ↓ Electrosorption process (電吸附)

- Electric-field-driven separation transportation of ions from bulk solution to the electrode
- Charge separation
   (capacitive ion storage as a supercapacitor)
   EDL formation

#### ↓ Highly porous electrode (多孔電極材料)

- High electrochemical stability
- Good electrical conductivity
- Good wetting behavior
- Large specific surface area
- Good pore accessibility for ion electrosorption



# 多孔電極之電化學反應

- Capacitive ion storage (EDL formation)/ and ion kinetics are the heart effects of CDI process.
- Other reactions need to be minimized.

S. Porada et al. Progress in Materials Science (2013)



#### 多孔電極材料





# 多孔電極材料在CDI的應用

#### Highly porous carbons as electrodes:

- Carbon aerogel
- Activated carbon
- Carbon nanofiber
- Activated carbon cloth
- Carbon nanotubes
- Graphene
- Ordered mesoporous carbon
- Hierarchical ordered carbon
- Other composite electrodes

#### Application to capacitive charge storage



# 奈米碳管 (Carbon Nanotubes)

- Carbon nanotubes have superior conductivity, excellent chemical inertness, and large sorption capacity
  - Carbon nanotube sheets (by chemical vapor deposition)
  - Polymer composite
    - poly(vinyl) alcohol (PVA)
    - Chitosan (CS)
    - Polyaniline
  - AC-CNTs composite







Tofighy and Mohammadi, 2010





## 規則性中孔洞材料(Ordered Mesoporous Carbons)

- 4 Mesoporous carbon (MC) are less affected by doublelayer overlapping to facilitate ion transport.
  - Synthesized using a self-assembly method via soft template
  - Good pore accessibility and ion selectivity



# 石墨烯 (Graphene)

Graphene (GE) has an ideal two-dimensional (2-D) carbon nanostructure.

- Graphene-like nanoflakes
- Reduced graphene oxide-ACs
- Graphene-CNTs
- Graphene-mesoporous carbon







Zhang et al, 2012

#### 階層孔洞碳電極 (Hierarchical Porous carbons)

- Hierarchical porous carbon (HPC) has a well-defined pore structure.
  - Macropores, mesopores, and micropores are well interconnected with a balanced ratio
  - Hierarchical activated carbon nanofiber
  - Hierarchical ordered mesoporous carbon
  - 3-D hierarchical porous carbon







# 選擇性電極 (Ion-Selective Electrode)

**4** Improvement of desalination efficiency and selectivity

- Carbon electrode coated with an ion-exchange polymer
- CNTs with sulfonic and amine functional groups
- **4** Born removal (activated carbon fiber, CDI)
- Selective removal of nitrate ions (MCDI)



Kim and Chio, 2010



# 電極材料的電容特性





The second second

# 比表面積與孔洞分布

Carbon	${S_{BET} \over (m^2/g)}$	${ m S}_{ m micro} \ (m^2/g)$	$S_{meso}$ $(m^2/g)$	$V_{tot}$ (cm <sup>3</sup> /g)	V <sub>micro</sub> (cm <sup>3</sup> /g)	$V_{meso}$ (cm <sup>3</sup> /g)	V <sub>meso/</sub> V <sub>tot</sub> (%)
Carbon aerogel	445	225	220	0.66	0.56	0.10	15.2
F-400 activated carbon	964	513	451	0.50	0.23	0.27	54.0
Wood activated carbon	662	457	205	0.43	0.21	0.22	51.1
Coal activated carbon	673	476	197	0.35	0.21	0.14	40.0
Coconut shell activated carbon	648	571	77	0.31	0.27	0.04	12.9
MWCNT/PVA	208	23	185	0.71	0.01	0.70	98.6
Highly mesoporous activated carbon	2105	850	1300	1.50	0.44	1.06	70.7
Highly microporous activated carbon	2162	1860	302	1.05	0.85	0.20	19.0

# 電容特性分析

#### Electrochemical characterization:

- Electrochemical impedance spectra (EIS)
- Galvanostatic charge/discharge curve (GC)
- Cyclic voltammetry (CV)



Voltammetric analyzer





電雙層電容器之電容行為



Activated carbon electrode 1 M NaCl solution.

#### 電化學穩定性



# 電容脫鹽之電吸附行為





#### Electrosorption performance

Batch mode
 experiment



- Continuous-flow (single-pass) mode experiment



#### 電容脫鹽之電吸附/脫附(充電/放電)曲線

Batch mode experiment

Regeneration of the activated carbon electrode in a batch experiment . The solution was 50 mL, 0.002 M NaCl solution with a flow rate of 10 mL/min. The applied voltage was 1.2 V



## 連續式電容脫鹽之曲線



Conductivity variation of 2000 ppm NaCl for multiple electrosorption-desorption cycles in CDI.

## 比表面積對於脫鹽之影響

Deionization of 500 ppm NaCl solution by activated carbon electrodes at 1.2 V and 5 mL/min in a continuous CDI system



✓ Carbon electrodes associated with higher specific surface area result in larger capacities for removal of NaCl from aqueous solutions.

✓ Generally, activated carbons operated in CDI have relatively low ion-accessible surface areas ( < 10% of BET surface area)</p>

#### 奈米碳管複合材料之脫鹽效能

#### Desalination experiments in bath mode CDI



Desalination of 1 mM NaCl solution using MWCNT and activated carbon electrodes at 1.2 V.

The presence of mesopores, facilitating ion transport, could be beneficial to ion electrosorption in CDI.

Carbon	MWCNT/ PVA	Activated carbon	
BET surface area (m <sup>2</sup> g <sup>-1</sup> )	208	964	
Micropore fraction (%)	11	53	
Electrosorption capacity (mg g <sup>-1</sup> )	13.07	6.03	
Surface utilization of BET surface area (%)	26.04	2.58	
Rate constant (min <sup>-1</sup> ), fitted by first-order kinetic model	0.073	0.045	
Energy consumption (kWh m <sup>-3</sup> )	0.038	0.155	

#### (Hou et al., Sep. Purif. Tech., 2014)

#### 活性碳之可控制孔洞分佈技術

#### **4** Two stage activated method

- KOH chemical activation
  - Activated with potassium hydroxide (KOH) under inert gas to form micropores accompanied with high surface area.
- CO2 physical activation
  - Gasified by carbon dioxide (CO<sub>2</sub>) to develop mesoporsity.









Commercial activated carbon

Activated carbon with controlled mesoporosity

# 高比表面積、高中孔洞活性碳之脫鹽效能

#### Desalination experiments in bath mode CDI



Mesopore to micropore ratio is a key factor to determine the CDI performance.

Yeh et al., Desalination, 2015



Manganese dioxide (MnO<sub>2</sub>)/activated carbon composite as high-performance CDI electrode



Liu et al., ACS Sustainable Chem. Eng, 2016

#### 電容去離子技術之應用潛力

+ CDI模組系統具有廣泛的適應性與良好的實用性

- 半鹽水淡化
- 家庭/工業再生水脫鹽
- 飲用水淨化(如水軟化)
- 微量污染物的去除
- 地下水中重金屬的去除
   (如鎘、鉻、砷等)
- 有價物質的選擇性回收



#### 脱鹽、低能耗、可能源回收

#### Continuous flow model of CDI

Reducing conductivity of water





- Desalination:
  - energy consumption
- Regeneration:
   energy recovery (>40%)



電吸附選擇性:硬水軟化

- Study the ion selectivity during the electrosorption process
  - Hydrated size
  - Ionic charge
  - Feed solution



	Ion	Test 1 (mM)	Test 2 (mM)	Test 3 (mM)	Test 4 (mM)
	$\mathbf{K}^+$	2	2	2	0.26
	Na <sup>+</sup>	2	4	6	10.57
	Ca <sup>2+</sup>	2	2	2	1.45
	$Mg^{2+}$	0	0	0	2.41

 $\label{eq:preferential} \begin{array}{l} \mbox{Preferential} \\ \mbox{electrosorption}: \\ \mbox{electrosorption capacity} \\ \mbox{follows the order of} \\ \mbox{Ca}^{2+} > Mg^{2+} > K^+ > Na^+ \end{array}$ 

Hou and Huang, Desalination, 2013

# 水回收/再生利用

Proposed processes for water reuse and recover of heavy metals from waste water

- Ultrafiltration: suspended solids
- Capacitive deionization: ionic species



廢水中重金屬之移除

0..4 \

 Electro-enhanced removal of copper ions from aqueous solutions by CDI
 Electrodeposition (> 0.8 V)
 Electrosorption (< 0.8 V)</li>



Removal of 50 ppm CuNO<sub>3</sub> solution at different applied voltages using activated carbon electrodes

Huang et al., J. Hazardous Materials, 2014



## 綠色能源技術媒合潛力

Capacitive deionization incorporates with renewable energy such as solar, wind, small-scale energy



# 結合生物電化學系統:產電-脫鹽技術

#### 4 Microbial fuel cell

- Electricity generation
- Wastewater treatment
- Capacitive deionization
  - Energy saving
  - Desalination

Sustainable water treatment process



Feng et al., Chemosphere, 2013

# 系統性整合RO與CDI技術

- Combined RO for seawater desalination (Jande et al., 2013; Minhas et al., 2014)
- Integrated pretreatment with CDI for RO reject recovery from water reclamation plant (Lee et al., 2009)



Ultrapure water from seawater using integrated RO-CDI system



Pretreatments using biological activated carbon (BAC) and BAC–ultrafiltration (UF)

# 電容脫鹽在水處理的應用

- **L** Treatment of brackish water (Xu et al., 2008)
- **Water softening** (Seo et al., 2009)
- **Froducing ultrapure water** (Lee and Choi, 2012)
- Selective removal of boron (Avraham et al., 2011) and nitrate ion (Kim and Choi, 2013)







Treating brackish water and recovering iodide from water.

Production of ultrapure water (10 mg/L NaCl influent)

Nitrate-selective electrode for the selective removal of nitrate

#### 地下水脫鹽與整治

Groundwater remediation (Framer et al., 1997)
Desalination in a remote location (Mossad et al., 2013)
Arsenic Removal from Groundwater (Fan et al., 2016)



Using CDI for inland brackish groundwater desalination in a remote location . RABBIT WA QLD Wilora NT ICE CODINCE SA CDI cell matrix Pre-filter Solenoid (SVI) Local Water Pipeline Solenoid (SV0) Citric-acid tank Solenoid (SV2) Solenoid (SV3)

Waste water Purified water

# 超純水的製造

# Membrane capacitive deionization (Lee and Choi, 2012) Combined RO and CDI (Jande et al., 2013)



# Puree (Korea)

- 4 Needed less energy for the desalination process because high pressure pumps are not required.
- Possible to make use of solar/wind power to power desalination units.
- More efficient for applications (withstand much higher temperatures than membranes)
- Far more efficient for the energy recovery than the membrane tech as the CDI modules act as EDLCs.

Model	TYPE	FLOW RATE(LPM)	SIZE(mm)	TDS REMOVAL	TEST CONDITION
Ecomite-U	Unit	0.03	160x160x40	> 85%	TDS 200ppm
Ecomite-M	Module	0.2~2	190x160x95	> 80%	TDS 1,000ppm
Ecomite-S	Unit/Module	0.03~2	565x650x8150	> 80%	TDS 2,000ppm





ECOMITE-S SERIES

# EST Water & Technologies (China)

#### Large scale CDI desalination modules

- Municipal wastewater reuse (60,000 m<sup>3</sup>/day)
- Coal mine Municipal wastewater reuse (5000 m<sup>3</sup>/day)
- Low energy consumption ~  $1.0 \text{ kWh/m}^3$



Low energy consumption
No chemicals added
Convenient operation
Long lasting service





# EST (爱思特)

- ▲ 電吸附水處理技術特點:運行成本低、耐受性強、 適應性強、水利用率高、無二次污染
  - 内蒙某电力集团循环排污水回用项目
  - 河北某化肥园区循环排污水回用工程
  - 山东某矿业集团矿井水利用工程
  - 山西某化工集团废水回用提质工程
  - 上海某钢铁集团冷轧废水零排放工程
  - 浙江宁波某再生水厂水质提升工程
    - (循环水补水、120000m<sup>3</sup>/d、产水率75%、
    - 氯离子去除率:85%、水电耗:0.75kWh/m<sup>3</sup>)
  - 宁波明耀火电厂深度除盐工程
  - 中石化山东某炼油废水回用工程

# 爱思特:電吸附脫鹽的實例

#### 電吸附模組的串聯



## 爱思特:電吸附脫鹽的實例



汗水處理站出流水的脫鹽處理

造紙廢水的脫鹽處理

水的除盐

方法与工程应用



# Voltea (The Netherlands)

#### Voltea CapDI system (MCDI)

- Cooling tower
- Wastewater reuse
- Domestic water softening
- Desalination of brackish water

- Energy efficient
- Chemical Free
- High water recovery (80-90%)
- Scalable
- Sustainable









# Aqua EWP (USA)

#### Electronic Water Purifier

- Commercial systems: US\$ 2500 ~ 12000
- One module: 1000~3000 ppm, 1~3.6 CMD



**US \$2500** 



US \$5000



US \$7500



US \$12500



- Feed salinity to 35,000 ppm,95% purification, 75% recovery
- Energy storage
- Pollutants Removed





# Test Reports of EWP

#### General Specifications

Flow Size:	WH-1 : 500 to 1,000 GPD
_imits: TDS	WH-1. 1,000 ppm
Recovery:	80%
Current:	2 amps max @110 VAC,
Size: unit	16"d x 12"w x 18" h



	Results		
Parameter analyzed			
Water source	RAW	<b>FINISHED</b>	WASTE
Calcium (Ca) ppm	3	0	5
Sodium (Na) ppm	203	40	484
Potassium (K) ppm	2	0	5
Boron (B) ppm	0.32	0.24	0.45
Carbonate (CO3) ppm	9	0	22
Bicarbonate (HCO3) ppm	393	88	919
Sulfate (SO4) ppm	25	5	62
Chloride (Cl-) ppm	63	13	148
Nitrate-N (NO3-N) ppm	0.019	0	0.032
Phosphorus (P) ppm	0.32	0.08	0.066
рН	8.08	7.26	8.01
Conductivity umhos/cm	806	170	1764
Hardness (CaC03)	11	0	17
Alkalinity (CaC03)	337	72	789
Total Dissolved Salts (TDS)	700	149	1648
SAR	26.2	8.1	51

#### Deeville



# Zero Liquid Discharge Process

#### **↓**97% Recovery? How?



#### 結論與建議

- 電容去離子技術為新穎的脫鹽技術,具有低能耗、操作簡易、高產水率、較無積垢問題、與環境友善 性等優點。
- 4 多孔電極材料的比表面積、孔洞分佈、電容特性在 電吸附脫鹽過程中,扮演重要的角色。
- ▲ 電容去離子技術具有廣泛的適應性與良好的實用性
  - ,可以應用在水淡化、硬水軟化、水再生利用(脫鹽)
     、重金屬去除、以及有價物質的選擇性回收等。
- ➡技術發展尚缺乏模組驗證, 朝向模組系統開發, 與商業化階段發展。



# 謝謝聆聽!

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