Overview of CO₂ capture and electrolysis technology in molten salts: operational parameters and their effects

Qiuji Zhu, a Yimin Zeng b and Ying Zheng a

Carbon capture and storage (CCS) technology is believed to be a promising solution for global CO₂ emission control and climate change. However, the application of CCS projects is facing a dilemma due to their negative cash flow. To address the challenge, it is critical to adopt an innovative technology that can capture and convert CO₂ simultaneously with satisfying efficiencies and can make a profit for the end users. Recently, molten salt CO₂ electrolysis that splits CO₂ into carbon and oxygen has been extensively studied. This study reviews the process mechanisms, the salt selection, and the effects of operating conditions, including temperature and voltage. In most reported articles, the CO₂ to carbon conversion efficiency reached at least 80%, and the current efficiency is over 90%, proving the promising potential of the molten salt CO₂ electrolysis method. Still, some aspects, such as the impurities’ influences and electrode corrosion, have not been thoroughly investigated. Therefore, some suggestions are recommended for future work.

Keywords: CO₂ capture; CO₂ conversion; Molten salt CO₂ electrolysis; CO₂ reduction; Carbon nanotubes.

1 Introduction

1.1 CO₂ emission

The first recognition of the negative impact of CO₂ can be traced back to the 1870s when European scientists concluded that carbonic acid, a by-product of rapidly expanded industrialization, contributed to acid rain and artificial warming. Later in 1936, lime scrubbing was first introduced to treat fuel gas, but this step was mainly targeted at the reduction of sulphur oxides. The research focusing on CO₂ capture and separation was primarily initiated and driven by commercial interests, such as urea yield boosting, carbonated drinks, and most importantly enhanced oil recovery (EOR). The CO₂ was sold at 50 USD per ton CO₂ for the EOR project, which essentially encouraged CO₂ capture. There were over

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It is undeniable that carbon dioxide capture commercial programs are tied closely to both global and national political considerations and further, complicated by technological developments. The debates between the industry sectors and governments have been taking place for decades. Since the 1970s, it has been witnessed that conferences and organizations increasingly promoted awareness of the harmful effects of CO₂ on all humankind and made countries collaborate to set up policies and projects. Interestingly, the 1970s was also the year when the first CO₂ capture project applied for EOR, showing timeline overlaps between concepts and application developments. The necessity of decarbonization and sustainability finally received special attention from policymakers and the public.

Carbon emissions are highly related to human activities. Thus, sorting out emission sources is the first step to adopting carbon capture projects. The pie chart in Fig. 1 provides a comprehensive breakdown of sectors contributing to global emissions. Energy-related sectors take the largest portion, 73.2%, where most energy used in this sector is supported by fuel combustion. The trend of energy-related CO₂ emissions by fuel has kept increasing in the past 21 years, as shown in Fig. 2. In 2021, the greenhouse gas emission rose to another new peak, reaching a total of 40 Gt (gigatons) CO₂. As coal-fired plants owned the cheapest operation cost, these plants guaranteed that coal was the leading fuel for energy generation and the top and stable CO₂ emission source. Oil and natural gas-related emission sources rebounded to 18.2 Gt, while coal emission sources reached a new-time peak of 15.3 Gt in 2021. The post-combustion is the most conventional and typical process in current thermal power plants. Although the CO₂ outlet level has a relatively lower concentration, only around 13 to 15%, post-combustion stands as a more competitive option because of final considerations regarding technological barriers and costs. Therefore, post-combustion CO₂ capture from power plants, especially coal-fired plants, has attracted substantial research interest. However, it is noticed that the Canadian Boundary Dam is, up to date, the only carbon capture and sequestration (CCS) project capturing post-combustion CO₂ from power generation. The gap between the CCS project and research interests not only results from unmatured technologies but is also affected by the massive costs and investments.

Many countries throughout the world actively initiate applicable policies for CO₂ reduction and heavily invest in research programs as well as major industrial-scaled CO₂ capture initiatives. Norway, for example, is the first country that implemented the carbon tax and operated the first large-scale Sleipner CCS project, applying monoethanolamide (MEA) absorption to purify natural gas containing 9% CO₂. Norway went through severe debates with the energy-intensive industry, revealing the complex impacts of the negotiated political economy on the project implementation. The Norwegian Sleipner project inspired the birth of many other projects, such as Salah CO₂ Storage in Algeria in 2004 and the Snøhvit CO₂ Storage Project in Norway in 2008. In 2014, Canada initiated the first industrial-scaled Boundary Dam CCS project in Saskatchewan to separate CO₂ from flue gases using amine absorption. A fraction of the captured CO₂ was sold and applied to EOR, and the rest was stored via the Aquistore project in Saskatchewan. The most recent CCS project, named Alberta Carbon Trunk Line, was built in Alberta, Canada, in 2020. MEA and methanol are used as absorbents to capture CO₂ from Sturgeon Refinery and Nutrient Redwater fertilizer plant. According to Global CCS data, Canada has four commercial CCS projects, considering its high carbon tax of $50 per tonne of carbon dioxide equivalent emissions.

1.2 CO₂ capture & conversion methods

Several CO₂ capture methods have been proposed and validated in the past decades. Fig. 3 shows the typical classification of the carbon capture methods, including chemical absorption, adsorption, membrane separation, and calcium looping. Molten salt electrolysisis, as an advanced method, can capture post-combustion flue gas and convert it into more valuable products to offset costs.

Amine absorption is the most mature and well-studied chemical absorption method for CO₂ capture. Its application can be traced back to the 1930s. Most industrial-scaled CO₂ capture plants, including the two post-combustion CO₂ capture plants operated at Boundary Dam and Petra Nova in Canada, employ the amine absorption method. However, solvent regeneration requests elevated temperatures, which causes a vast energy penalty. In addition to energy consumption, the corrosivity and high volatility of amine solvents can cause various operational issues. Adsorption...
is another method that has been successfully applied in industrial-scale CO₂ capture plants, such as Air Products facilities for hydrogen production.⁴,¹⁸ Natural sorbents, such as natural zeolites, natural plants (such as fruit shells), and coal-based materials, can be selected to perform adsorption, or human-made sorbents, such as activated carbon, metal-organic frameworks (MOFs), and zeolite, can adsorb CO₂.²⁴–²⁶ So far, this pathway faces more challenges than absorption as the overall performance is even worse: high material costs (especially for MOFs), capacity loss during the process, high regeneration cost, and low adsorption capability (3–11 wt%), etc.²¹ Other promising methods include membrane separation, calcium looping, and cryogenic separation.²⁵

The above-mentioned conventional methods produce purified CO₂ and thus raise the same problem, which is the cost. The amount of purified CO₂ used for EOR and other industries is limited, and a large portion of captured CO₂ has to be stored, which leads to a negative cash flow. It explains the fact that there are only a few CCS projects, practically of which are funded by governments. Taking the Canadian Quest plant as an example, it requires average funding of 30 million annually for operation.¹⁵ The Petra Nova project is another example, which captured the power plant’s post-combustion CO₂ using amine absorption and sold for EOR. However, it was abruptly closed its business after only three years of operation due to imbalanced costs.²² Due to its profit-driven nature, private corporations or even governments would only start to or continue operating CCS projects if they can generate profits and cover the cost of the carbon tax and other possible budgets.

Numerous carbon conversion methods have been reported and well-studied.²³,²⁷–³⁰ A variety of conversion methods, such as photochemical, biological, and hydrogen transformation pathways, are being developed for industrial applications.⁶,¹¹–¹⁴ The advantage of these methods is that they can obtain hydrocarbons and other marketable products (such as dimethyl carbonate, synthesis gas, carboxylic acids, methane, etc.) that are significantly more valuable than pure CO₂. However, the deployment of these methods still faces critical challenges, such as evaporation occurring under high-temperature gas inlets, difficulty in final product separation, requirement on high CO₂ concentration feedstock. Moreover, some of the proposed methods likely suffer the unsatisfying production rates and the limitation of equilibrium and CO₂ solubility. For instance, the conversion of CO₂ to dimethyl carbonate was only around 1–5% due to the chemical equilibrium limitation.²³ It was also reported that the production using alkaline electrolytes, such as KOH, is restricted to the conversion of CO₂ to CO less than 50% due to the formation of carbonates and bicarbonates.²⁷

Molten salt CO₂ electrolysis is a novel technology combining CO₂ capture and conversion. The development of the method was initiated in the 1960s and has quickly expanded since the 2000s. This method allows to capture CO₂ from hot flue gas, and the captured CO₂ can be directly converted in the molten salt electrolyte at high temperatures into valuable products, such as carbon, carbon monoxide, and O₂.³⁵ As CO production requires more energy consumption and presents lower current efficiency, CO would
not be an ideal product. Researchers show more interest in producing high-quality carbon materials and manipulating their nanostructures.

As its electrolyte contains zero water and targets carbon formation, molten salt electrolysis can result in a single solid carbon product with high current efficiency and avoid complex products with tough or multiple separations. Additionally, the in situ conversion of CO$_2$ to value-added products prevents extra costs after carbon capturing, such as CO$_2$ transportation costs, debatable and uncertain storing, maintenance costs, etc. A molten salt CO$_2$ electrolysis plant is estimated to bring a net profit of $50,000 per ton of captured CO$_2$ for a power plant when the final electrolysis product is carbon nanotubes (CNTs). One common approach for growing CNTs is chemical vapour deposition (CVD), which anticipates requiring at least 1440 MJ and emitting 28.55 kg CO$_2$e for producing one gram of CNTs. Therefore, this profit and benefits can drive the molten method to potential scale-up plants and promote the carbon capture installed in general power plants, outweighing the financial burdens that the above-mentioned conventional methods have. This report will focus on this electrolysis method for carbon capture and conversion.

### 2 Molten salt CO$_2$ electrolysis system

Molten salt CO$_2$ electrolysis is used to capture CO$_2$ and electrochemically convert the captured CO$_2$ into valuable products, including solid carbon, oxygen, and carbon monoxide. The key components of the system contain electrolytes, electrodes, and an external power supply, as shown in Fig. 4. Electrolytes are melted salts containing zero water at a temperature higher or equal to melting points, and they are responsible for capturing inlet CO$_2$ and transferring ions and electrons. Product evolution and deposition occur on the electrode surfaces. In general, the inlet CO$_2$ is electrochemically split into oxygen and carbon or oxygen and carbon monoxide under harsher high-temperature conditions.

![Fig. 4](image)

**Fig. 4** A schematic of a molten salt electrochemical system towards carbon deposition.

Capture: $\text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_2^2^-$  
Cathode: $\text{CO}_2^2^- + 4\text{e}^- \rightarrow \text{C} + 3\text{O}_2^2^-$  
Anode: $2\text{O}_2^- \rightarrow \text{O}_2 + 4\text{e}^-$  
Overall: $\text{CO}_2 \rightarrow \text{C} + \text{O}_2$

General temperature range: 400 – 900 °C  
Electrolysis technique: constant voltage or constant current
CO₂ is firstly absorbed by O²⁻ or CO₃²⁻ ions and turned into carbonate or dicarbonate ions. Then, CO₃²⁻ ions primarily follow a single-step reduction on the cathode through a 4-electron transfer, resulting in carbon deposition on the cathode and releasing oxygen ions. However, at higher temperatures, CO₃²⁻ ions tend to undergo a 2-electron transfer instead of a 4-electron to form CO as the final product on the cathode due to the fact that the generation of CO is more thermodynamically favourable than the formation of carbon. Note that the movement of carbonate ions is against the electric field since the reduction reaction exclusively happens on the cathode, and the driving force of concentration gradient overweighs the repulsion force of the electric field. The decreased carbonate ions at a cathode zone were reported in LSV tests, and the reduction of carbonate ions was found to weaken the electric current during constant voltage electrolysis. However, the effects of the electric field have never been reported nor compared to the concentration driving force. This topic should be investigated in the future to understand the cathodic electrolysis mechanism in a continuous operation.

The produced oxygen ions can either remain in the system to enhance CO₂ absorption or be oxidized as oxygen gas and then released from the anode. The whole electrolysis takes place in molten salt, which involves zero water. This can significantly avoid the competitive water split reaction. Thus, the current efficiency is improved and remains over 80%. Also, the formation of a complex hydrocarbon mixture is also avoided, so the product separation is much easier. As a result, the conversion of CO₂ to carbon and oxygen is more competitive as the current efficiency can exceed 90%. However, when CO and oxygen are the desirable products, the process cannot achieve 90% carbon conversion at equal conditions. Thicker CO₂ inlet concentration (over 14%) and more extreme temperatures (at 900 °C) were required to push CO production to 90% conversion. Additionally, the current efficiency for CO manufacturing purposes was relatively low, only around 36.9%, and this can be explained by unwanted side reactions. More detailed mechanisms and reactions are discussed in the later section.

Table 1 lists the molten salt CO₂ electrolysis reported since 2019, and the records before 2019 can be found in Jiang’s review. Additionally, the generated records focus on the cases utilizing carbonate electrolytes, and the reasons will be discussed in detail in the electrolyte section. The trend between 2019 and 2022 can be classified into 3 major types:

**Table 1** A list of molten salt CO₂ electrolysis focusing on carbonates electrolytes since 2019

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>T (°C)</th>
<th>Cathode</th>
<th>Anode</th>
<th>Current/current density</th>
<th>Carbon related products Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂CO₃</td>
<td>770</td>
<td>Galvanized steel; Ni-Cr</td>
<td>Ni-Cr; galvanized steel</td>
<td>1 A</td>
<td>Multi-walled carbon nanotubes (MWCNTs); CNTs</td>
</tr>
<tr>
<td>Mg₂CO₃</td>
<td>650</td>
<td>Ni</td>
<td>Graphite</td>
<td>0.2–1 A cm⁻²</td>
<td>Carbon particles</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>770</td>
<td>Cu</td>
<td>Ir-Pt</td>
<td>0.2 A cm⁻²</td>
<td>Carbon nanonions; CNTs</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>770</td>
<td>Muntz brass sheet</td>
<td>Nichrome sheet</td>
<td>0.2 A cm⁻²</td>
<td>Carbon nanotubes (CNTs)</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>670</td>
<td>Muntz brass sheet</td>
<td>Inconel</td>
<td>-</td>
<td>CNTs</td>
</tr>
<tr>
<td>Li₂CO₃-Na₂CO₃-K₂CO₃</td>
<td>450–650</td>
<td>Ni</td>
<td>SnO₂</td>
<td>0.2–4 A g⁻¹</td>
<td>Activated carbons; CO; hydrocarbons, H₂</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>225–475</td>
<td>Ti</td>
<td>Graphite</td>
<td>-</td>
<td>CNTs</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>770</td>
<td>Muntz brass as</td>
<td>Inconel 718; Nichrome; Incoloy Graphite</td>
<td>0.5 A</td>
<td>Fe₃C; CNTs</td>
</tr>
<tr>
<td>LiCl·Li₂CO₃·LiBO₂</td>
<td>550</td>
<td>Ni</td>
<td>Graphite</td>
<td>25–100 mA cm²</td>
<td>CO</td>
</tr>
<tr>
<td>LiCl·Li₂CO₃·LiBO₂</td>
<td>550</td>
<td>Ni</td>
<td>Graphite</td>
<td>-</td>
<td>Carbon nanofibers (CNFs); CO Graphene; CNTs</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>730</td>
<td>Galvanized steel</td>
<td>Pt</td>
<td>-</td>
<td>43</td>
</tr>
<tr>
<td>Li₂CO₃·K₂CO₃·Na₂CO₃</td>
<td>650</td>
<td>NiO-CO₃O₄</td>
<td>Ni₁₀Cu₁₁Fe</td>
<td>10 mA cm⁻²</td>
<td>NiCo@g-c powder</td>
</tr>
<tr>
<td>Li₂CO₃·K₂CO₃·Na₂CO₃</td>
<td>650–750</td>
<td>Ni</td>
<td>Pt</td>
<td>5–100 mA cm⁻²</td>
<td>Graphite</td>
</tr>
<tr>
<td>LiCl·Na₂CO₃-K₂CO₃</td>
<td>710–850</td>
<td>Ni</td>
<td>Ni₁₀Cu₁₁Fe</td>
<td>3 V</td>
<td>Carbon particles</td>
</tr>
<tr>
<td>Li₂CO₃·K₂CO₃·Na₂CO₃</td>
<td>450</td>
<td>Ni</td>
<td>Pt-Ti</td>
<td>100 mA cm⁻²</td>
<td>Electrolytic carbon</td>
</tr>
<tr>
<td>LiCl·Na₂CO₃-K₂CO₃·Na₂CO₃</td>
<td>750</td>
<td>Ni</td>
<td>Ni₁₀Cu₁₁Fe</td>
<td>200 mA cm⁻²</td>
<td>CNTs</td>
</tr>
<tr>
<td>LiCl·Na₂CO₃-K₂CO₃·Na₂CO₃</td>
<td>770</td>
<td>Ni</td>
<td>Ni₁₀Cu₁₁Fe</td>
<td>8–600 mA cm⁻²</td>
<td>CNTs</td>
</tr>
<tr>
<td>LiCl·Na₂CO₃-K₂CO₃·Na₂CO₃</td>
<td>750</td>
<td>Ni</td>
<td>SS</td>
<td>7.5 A</td>
<td>Carbon sphere</td>
</tr>
</tbody>
</table>

Note: this table includes reported molten salt electrolysis since 2019 and focuses on carbonate electrolytes. Reports prior to 2019 can be found in Jiang’s review.
1. Production of specific carbon nanostructure by modifying operation conditions and electrolysis system components;  
2. Method and equipment improvements, including separation improvement and reactor design;  
3. Expansion of molten salt CO2 electrolysis to produce other materials, such as hydrocarbons.  

2.1 Electrochemical conversion mechanism  

In a molten salt system, the reactions on the surface of electrodes are monitored closely via cyclic voltammetry (CV) measurements. At sufficiently high temperatures (a temperature higher than the melting points of selected salts), the desired electrochemical reactions for the carbon formation are shown below:  

$$\text{Cathode: } \text{CO}_3^{2-} + 4e^- \rightarrow C + 3\text{O}^2- \quad (1)$$  
$$\text{Anode: } 2\text{O}^2- \rightarrow \text{O}_2 + 4e^- \quad (2)$$  

Cyclic voltammetry (CV) tests are employed to record the reduction of CO$_3^{2-}$ at a cathode, expressed in eqn (1). As the peak of electric current declines quickly, there is deficient CO$_3^{2-}$ reaching the cathode. Additionally, a slow scan linear sweep voltammetry (LSV) test measures the slow diffusion of oxide ions (O$_2^-$). The sluggish diffusions of CO$_3^{2-}$ and O$_2^-$ limit the electrolysis.  

$$\text{CO}_2 + \text{O}_2^- \rightarrow \text{CO}_3^{2-} \quad (3)$$  
$$\text{CO}_3^{2-} + \text{CO}_2 \rightarrow \text{C}_2\text{O}_5^{2-} \quad (4)$$  

Only at severe operating conditions, for example, at 1000 °C shown in Fig. 5, CO instead of carbon is produced due to lower Gibbs free energy for producing carbon. Temperature is one of the critical factors. At a temperature exceeding 950 °C in molten Li$_2$CO$_3$, CO production is thermodynamically favoured over carbon deposition. For instance, at 1200 °C in Li$_2$CO$_3$, the electrochemical potential, calculated from Gibbs free energy for carbon production, is about 1.1 V, while CO formation requires only 1.0 V.  

$$\text{CO}_3^{2-} + 2e^- \rightarrow \text{CO} + 2\text{O}^2- \quad (5)$$  

Side reactions have also been reported. Kaplan documented the metal intercalation reaction since the carbon cathode swells while there are no visible changes to the graphite when used as the anode. Tang observed the sparks resulting from alkaline metal and water during the sample wash, indicating the side reaction of metal deposition in eqn (6). Cyclic voltammetry (CV) tests also reveal the two reduction peaks representing carbon and metal deposition, respectively, by eqn (1) and (6). Heat deposition of carbonates is commonly observed, shown in eqn (7). Then, metal oxides can be ionic to also provide oxide ions for CO$_2$ capture in eqn (8). In order for eqn (8) to take place, metal oxides must be molten or dissolved in molten salts.  

$$\text{M}^+ + e^- \rightarrow \text{M} \quad (M = \text{Li, Na, Ca or K}) \quad (6)$$  
$$\text{M}_n\text{CO}_3 \rightarrow \text{CO}_2 + \text{M}_n\text{O} \quad (7)$$  
$$\text{M}_n\text{O} \text{ (liquid) } = \text{M}^{n+} + \text{O}_2^- \quad (M = \text{Li, Na, Ca or K}) \quad (8)$$  

The formed metals can directly react with CO$_2$ gas to generate CO, as shown in eqn (9).  

$$n\text{M} + \text{CO}_2 = \text{CO} + \text{M}_n\text{O} \quad (M = \text{Li, Na, Ca or K}) \quad (9)$$  

When the temperature exceeds 850 °C, CO and CO$_2$ start to be co-produced. But if the applied current density or temperature is not high enough, the formed CO could be
decomposed to carbon and \( \text{CO}_2 \) via the Boudouard reaction.\(^{63} \) If CO is the desired final product, molten salt electrolytes, such as LiCl-Li_2O, should be selected to avoid the Boudouard reaction.\(^{67} \)

\[
2\text{CO} \rightarrow \text{CO}_2 + \text{C} \quad (10)
\]

Due to the reactions shown in eqn (1), (5), and (8), \( \text{O}^2- \) accumulates in the system and is then driven by an applied electric field to form oxygen on the anode surface. But if excessive \( \text{O}^2- \) is accumulated, it is possible to corrode alumina or zirconia container or electrode.\(^72 \) If carbon is used for the anode, excessive \( \text{O}^2- \) could react with the carbon to produce \( \text{CO}_2 \). Then, the carbon anode would degrade quickly.\(^{31,63,67} \) Deposited carbon on the cathode also undergoes re-oxidation reactions with \( \text{O}^2- \). In the cases of limited \( \text{O}^2- \) in molten chlorides, carbon could react with carbonate ions to re-produce \( \text{CO}_2 \).

\[
\text{C} + n\text{O}^2- \rightarrow \text{CO}_n + 2n\text{e}^- \quad (n = 1 \text{ or } 2) \quad (11)
\]

\[
\text{C} + 2\text{CO}_3^{2-} \rightarrow 3\text{CO}_2 + 4\text{e}^- \quad (12)
\]

Finally, the last step is to collect and/or wash the products. Carbon samples can be washed with water or acid solution, such as HCl, and the concentration of the acid can also affect the element composition of the final product. With a higher concentration of HCl, more impurities, including carbonates, oxides, and metals, in carbon samples can be washed away. For example, carbon samples obtained at the same operation conditions could have a maximum of about 13 weight% more carbon content. In comparison, around 9 weight% less oxygen when the sample is washed in 8.7 mol L\(^{-1} \) HCl compared to 2.3 mol L\(^{-1} \) HCl.\(^73 \)

Molten salt \( \text{CO}_2 \) capture and electrochemical transformation is a complex system. Thus, there is a list of parameters or components affecting the performance, products, energy consumption, etc. The parameters include cell components (electrolytes and electrodes), feeding stream, and operation conditions (power supply and temperature). In most cases, the carbon products are amorphous. A small number of impurities may also be identified depending on different operation conditions.\(^{35,76,73} \) Therefore, carbons of different morphologies can be obtained by adjusting the operating conditions.

2.2 Electrolytes

In addition to molten salts, electrolytes can be replaced by aqueous solutions, ionic liquids, and solid electrolytes. Different electrolytes exhibit various selectivity, products, and efficiency. Electrolytes are crucial for collecting \( \text{CO}_2 \) from the incoming gas stream and transferring ions. Aqueous solutions are impractical when served as electrolytes due to a number of significant disadvantages, including poor electrochemical windows, water splitting, limited solubility, and slow reaction kinetics.\(^{35,75} \) Ionic liquids show excellent chemical stability, high \( \text{CO}_2 \) solubility, and high conversion yield, but the high cost and low reaction kinetics hinder them from commercial-scaled applications.\(^{35,76} \) Solid electrolytes have an overall higher current efficiency, but their specific conductivity is less than half that of molten salt electrolytes.\(^62 \) Even worse, sulphur impurities negatively affect the solid electrolytes, making this type of electrolytes unfavoured for capturing power plant flue gas commonly containing sulphur compounds.\(^62 \)

Many researchers believe high-temperature molten salts are the optimal electrolyte because of their satisfying properties. Molten salts present low toxicity, high heat capacity, wide electrochemical operating window, high ionic conductivity, and low costs due to abundant availability.\(^77 \) Furthermore, the same metal oxide components, for example, \( \text{Li}_2\text{O} \), show an enhanced \( \text{CO}_2 \) absorption ability in the molten phase compared to the solid phase.\(^78 \) Impurities from flue gas, \( \text{SO}_2 \) and \( \text{NO}_2 \), can be converted into valuable S/N-doped carbon materials.\(^78,79 \) Selecting a molten salt electrolyte is considered more crucial than choosing an electrode since electrolytes have a greater impact on the final carbon product.\(^80 \) Wang observed that carbonates and oxides impacted the nanostructures of resulted carbon, while five different cathodes produced little changes to the final product.\(^80 \)

Carbonates, chlorides, and oxides containing \( \text{Li}^+, \text{Ca}^{2+}, \text{Na}^{+}, \text{K}^+ \) are the most widely researched electrolytes due to their wide electrochemical windows and good \( \text{CO}_2 \) solubility.\(^62 \) Carbonates and chlorides take up a large portion of salts, and oxides are commonly used as additives, ranging from 1 wt% to 30 wt%. The types of salts present distinct advantages and drawbacks, and as a result, they are commonly mixed together to achieve optimal performance, such as lower melting points. But before mixing, it is essential to identify the features of salts first.

2.2.1 Carbonates or chlorides. Mixed salts frequently present lower melting temperatures than pure constituents. Chlorides show even lower melting points than carbonates. LiCl–KCl eutectic is 353 °C, lower than general carbonates listed in Table 2.\(^81 \) However, it should be noted that operating temperatures are not the only factor contributing to total energy consumption, as voltage supply also take a large portion of energy input. With higher temperatures, the voltage requirement for the reaction is reduced. For instance, the energy consumption is 16.3 kW h kg\(^{-1} \) of carbon

| Table 2 Melting points of carbonates and their mixtures\(^83 \) |
|---------------------------------|---------|
| Salt system                    | Melting point (°C) |
| \( \text{Li}_2\text{CO}_3 \)    | 723     |
| \( \text{Na}_2\text{CO}_3 \)    | 854     |
| \( \text{K}_2\text{CO}_3 \)    | 891     |
| \( \text{Li}_2\text{CO}_3 - \text{Na}_2\text{CO}_3 \) (52–48 mol%) | 501     |
| \( \text{Li}_2\text{CO}_3 - \text{K}_2\text{CO}_3 \) (62–38 mol%) | 498     |
| \( \text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3 \) (56–44 mol%) | 716     |
| \( \text{Li}_2\text{CO}_3 - \text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3 \) (43.5–31.5–25 mol%) | 397     |
| \( \text{K}_2\text{CO}_3 - \text{MgCO}_3 \) (57–43 mol%) | 460     |

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produced at 650 °C but 31.4 kW h kg⁻¹ at 450 °C. CO₂ solubility in chlorides is extremely low, resulting in low mass transfer. As shown in Fig. 6, molten chlorides like LiCl–KCl have poor CO₂ absorption. Thus, chlorides need to team with oxides or carbonates to improve carbon absorption and conversion. Compared to carbonate electrolytes with oxide additives, the chlorides with oxide additives show faster CO₂ absorption and reach equilibrium within 2 h, which demonstrates a better CO₂ absorption. The reaction of Li₂O and CO₂ resulting in Li₂CO₃ is responsible for the high absorption capacity. The conversion efficiency for Li₂O into Li₂CO₃ almost doubled in molten chloride electrolyte (around 94%) compared to that in molten carbonate electrolyte (about 45%), indicating the molten salt composition affects both the absorption thermodynamics and the kinetics for Li₂O conversion. This change in the oxide conversion efficiency can be explained by the low activity of Li₂O in the molten carbonates and the strong chemical interaction between CO₂ and carbonates. The latter slows down the CO₂ diffusion rate for desired conversion reactions.

Another difference between carbonates and chlorides is the solubility of additives, such as CaO and Li₂O, which later lead to different reaction mechanisms. CaO or Li₂O is soluble in CaCl₂ but hardly dissolves in carbonates. Chloride electrolytes typically contain oxide additives. However, they still have overall fewer oxygen ions than carbonate electrolytes, which can reduce the adverse effects of the consumption of deposited carbon as indicated in eqn (11) and (12). However, when CO₃²⁻ is wholly consumed in chlorides, the current density reaches nearly zero. It indicates neither pure chlorides are suitable for CO₂ splitting, nor chlorides with additives are stable for long-term electrolysis. A more detailed and comprehensive review focusing on chloride salts can be found in Díez’s report, including how the salts and added biomass serve as templates for the formation of micro-pores, which resulted in various carbon nanostructures.

For carbonate electrolytes, the solubility of its oxide or additives leads to two different mechanisms. For insoluble oxides (such as CaO), the primary electrolysis reaction refers to the conversion of carbonates (CaCO₃) into corresponding oxides (CaO) and carbon deposition, and O₂ formation. Solid CaO on the cathode surface is difficult to absorb CO₂ and convert itself back into molten CaCO₃ to complete the loop. Therefore, carbonates, whose oxides are insoluble, keep being consumed over time at high operation temperatures, and the oxides and carbon co-deposit on the cathode surface. The latter mechanism is for soluble oxides (such as BaO), where carbonate ions are converted to carbon and O₂. In this case, BaO dissolves in the electrolyte and provides oxide ions to continuously capture CO₂ and transfer back to fresh BaCO₃. Only carbon deposits on the cathode surface. Similar discoveries are observed where CaO and Li₂O solidify and cover cathodes, hindering CO₂ absorption and weakening electrolysis. Kanai et al. are among the few research groups investigating the mass transfer in molten carbonates, as shown in Fig. 7. Elevated temperature enhanced CO₂ solubility in both binary (Li–K) and ternary (Li–K–Na) molten carbonates, and the solubility values of these two types of carbonates are close to each other. The dissolution of CO₂ in molten salts can be classified into two categories: physical and chemical dissolution. The chemical dissolution is expressed in eqn (3) and (4) while the physical dissolution is
carbonates.88,89 This ratio again indicates the necessity of Li, Ca, and Ba carbonates than in Na or K carbonates, as conditions than Na or K. Carbon deposition is less difficult in Li, Ca, and Ba metal depositions require more challenging decomposition, and quality of carbon produces. Furthermore, metal depositions generally require more energy input and sacrifices current efficiency. Li or Ca carbonates are more stable and suitable than Na or K-containing carbonates, considering the deposition potentials, heat decomposition, and quality of carbon produces. Furthermore, Li, Ca, and Ba metal depositions require more challenging conditions than Na or K. Carbon deposition is less difficult in Li, Ca, and Ba carbonates than in Na or K carbonates, as shown in Table 4.34,60 Li2CO3 conductivity is 6 S cm−1, 2 times higher than Na2CO3 and 3 times higher than K2CO3 at their melting points.74 Its higher conductivity lowers ohmic loss and thus enhances reactant or electron mass transfer. Thanks to various properties, a mixture of carbonates containing different cations is commonly applied to offer optimum behaviour.

Li2CO3 can decompose at temperatures far lower than the melting point, while CaCO3 is chemically stable as its decomposition temperature exceeds its melting point (825 °C).41 As previously discussed, temperatures over 825 °C are more favourable for CO generation than carbon production. Under the same operating conditions, the CO2 capture percentage in CaCl2–CaO can be approximately 17 times higher than in LiCl–Li2O because Ca has higher reduction energy thermodynamically than Li does.67 The relatively low conductivity of BaCO3 and low basicity of BaO can improve the cell voltage during electrolysis and limit anode corrosion.39 But BaCO3 is an uncommon option due to its high cost and toxicity.41

Different cations in carbonates also lead to various carbon nanostructures. Li+ and Ba2+ are expected to promote the formation of CNTs, but K+ hinders the formation of carbon nanostructures.80,91 It is further evidence that electrolytes containing more than 50 wt% of Na or more than 30 wt% K carbonates inhibited CNTs growth but supported the development of carbon nano-scaffolds (CNS).53 Overall, previous studies supported lithium-related salts because of their exceptional qualities.

### 2.2.3 Additives

The additions have been used to fine-tune carbon nanostructures and improve CO2 absorption. The additions can be classified into two groups: carbonate heat decomposition (CaO, Li2O, and BaO) and foreign ones (CuO, CoO, ZnO, Fe2O3/Fe3O4 etc.). The additions that have been well studied include CaO, Li2O, CuO, CoO, ZnO, and Fe2O3/Fe3O4.81,92 Metal cations of the additives can serve as nucleation sites and influence the nanostructures of carbon and improve the CO2 capture rate due to chemical bonding between acidic CO2 and alkaline absorbents.76 However, the overall CO2 capture and conversion efficiency may not

<table>
<thead>
<tr>
<th>Molten salt</th>
<th>10−106</th>
<th>S_{REF} \left( \text{m}^2 \text{g}^{-1} \right)</th>
<th>Pore volume \left( \text{cm}^3 \text{g}^{-1} \right)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li2CO3−Na2CO3−K2CO3</td>
<td>0.86</td>
<td>897.4</td>
<td>0.862</td>
<td>4.62</td>
</tr>
<tr>
<td>2 mol% Li2CO3−LiCl−KCl</td>
<td>0.67</td>
<td>113.9</td>
<td>0.279</td>
<td>9.97</td>
</tr>
<tr>
<td>2 mol% Ca2CO3−LiCl−KCl</td>
<td>0.72</td>
<td>157.9</td>
<td>0.125</td>
<td>3.98</td>
</tr>
</tbody>
</table>

(C∗ is CO2 solubility, R is the gas constant, T is temperature, N is Avogadro’s number, A is the contacting surface area, and γ is the surface tension of the molten salts).

Fig. 6 shows that molten carbonates also have higher current efficiency at the same current rate, indicating that using carbonates could prevent several side reactions that occur with chlorides, particularly the development of chlorine gas.

Electrolyte compositions can significantly affect the properties of produced carbon in terms of morphology, surface area, pore volume, and conductivity. In Table 3, Deng’s research shows that the specific surface area and pore volume of carbon obtained from molten carbonates can be 8 times larger than those from molten chlorides.76 As discussed above, carbonates also hold more remarkable absorption ability and stability. These essential characteristics outweigh their drawbacks, which lead to favouring carbonates over chlorides in molten salt electrolysis. Therefore, the cation selections section focuses on carbonate salts and their related research.

#### 2.2.2 Cation selections

The choice of alkaline metal cations has a considerable impact on the reaction and end products, in addition to the broad types between carbonates and chlorides, due to their thermodynamic characteristics and cation sizes. The following discussion mainly focuses on carbonate electrolytes. Metal cations dominate the properties in the carbonate system and can be reduced to metal elements during electrolysis. Metal deposition has a contradictory influence on electrolysis. On the positive side, metal particles can act as active sites for carbon deposition. However, metal deposition generally requires more energy input and sacrifices current efficiency. Li or Ca carbonates are more stable and suitable than Na or K-containing carbonates, considering the deposition potentials, heat decomposition, and quality of carbon produces. Furthermore, Li, Ca, and Ba metal depositions require more challenging conditions than Na or K. Carbon deposition is less difficult in Li, Ca, and Ba carbonates than in Na or K carbonates, as shown in Table 4.34,60 Li2CO3 conductivity is 6 S cm−1, 2

Table 4 Deposition (vs. CO2/CO2) of alkali and alkaline earth metals via eqn (7)−(8) and carbon via eqn (1) at 600 °C (ref. 41)

<table>
<thead>
<tr>
<th>Molten salt</th>
<th>Alkali metal (V)</th>
<th>Carbon (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li2CO3</td>
<td>2.964</td>
<td>1.719</td>
</tr>
<tr>
<td>Na2CO3</td>
<td>−2.546</td>
<td>−2.551</td>
</tr>
<tr>
<td>K2CO3</td>
<td>−2.612</td>
<td>−3.083</td>
</tr>
<tr>
<td>CaCO3</td>
<td>−3.033</td>
<td>−3.349</td>
</tr>
<tr>
<td>BaCO3</td>
<td>−3.069</td>
<td>−1.992</td>
</tr>
</tbody>
</table>

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enhance, considering the complex effects of oxide ions in metal oxide additives.\textsuperscript{64,69,83}

When Li\textsubscript{2}CO\textsubscript{3}, CaCO\textsubscript{3} or BaCO\textsubscript{3} are used, LiO, CaO, and BaO are formed as thermal decomposed products. For instance, 1 mol Li\textsubscript{2}CO\textsubscript{3} could generate up to 0.0222 mol LiO at 750 °C in the air without the influence of electrochemical reactions.\textsuperscript{80} As shown in Table 4, the voltage required to reduce sodium ions to sodium is close to that required to deposit carbon. Since potassium deposition potential is lower than carbon deposition potential in molten K\textsubscript{2}CO\textsubscript{3}, a large portion of electrolysis current would be wasted on reducing potassium if carbon is the desired product. This also suggests the loss of electrolytes when metals deposit on the cathode. LiO, as a decomposed product or a manual additive, serves as an intermediate for capturing CO\textsubscript{2}, ensuring continuous operation, and avoiding wasting current on undesired metal deposition. Because Li\textsubscript{2}CO\textsubscript{3} holds a relatively low potential for carbon deposition and a high potential for metal deposition, LiO can continuously absorb carbon dioxide and form Li\textsubscript{2}CO\textsubscript{3}, and regenerate oxides after carbon deposits. In this continuous operation, LiO is stable as it can avoid being reduced to Li metal as long as the electrochemical window is wisely chosen. Thus, in case Li\textsubscript{2}CO\textsubscript{3} is selected as the electrolyte, carbon would be produced without deposition of metal Li so that the molten salt system remains stable and continuous addition of salts is avoided. This viewpoint was supported by the experimental results that the alkalinity of molten salt Li\textsubscript{2}CO\textsubscript{3}–Na\textsubscript{2}CO\textsubscript{3}–K\textsubscript{2}CO\textsubscript{3} remained steady during continuous operations, and no LiO accumulation could be achieved in the system.\textsuperscript{35}

Furthermore, Li\textsuperscript{+} is a critical component for molten salt electrolysis carbon deposition. Tests on CV performed to track the peaks in carbon reduction provide evidence for this claim. Without Li\textsubscript{2}CO\textsubscript{3}, the Na\textsubscript{2}CO\textsubscript{3}–K\textsubscript{2}CO\textsubscript{3} electrolysis experiment showed no carbon reduction peak at 750 °C. Adding more CaO enhanced CO\textsubscript{2} absorption with a linear correlation of about 1 between metal oxides and CO\textsubscript{2}.\textsuperscript{81} However, this conversion was reduced by 20% when the temperature increased from 550 to 600 °C because the carbonation formation is endothermic, which is not favoured at a higher temperature. LiO was also observed to absorb more CO\textsubscript{2} with increasing weight percentage, and the optimum trial reached a maximum of 0.1105 g\textsubscript{CO\textsubscript{2}} g\textsubscript{metal}\textsuperscript{−1}, conducted with 8 wt% additive at 923 K under 101.3 kPa.\textsuperscript{93} However, it should be highlighted that these gas solubility data was obtained without electrolysis, and section 2.2.1 and below contents discuss how metal oxide additives solidify on the cathode and hinder absorption due to additives’ poor solubility in electrolytes.

Foreign metal oxides serve as necessary nucleation sites for special carbon nanostructure growths, especially CNTs growth. In fact, one of the most popular research topics focuses on molten salt carbon dioxide capture and electrolysis to produce CNTs and other special nanostructures shown in Fig. 8. Various metal oxides have been tested and examined for carbon nanostructures. Zn or ZnO additives were favourable for carbon nanofiber formation.\textsuperscript{92} Fe\textsubscript{2}O\textsubscript{3} is another popular additive. In some cases, the electrodes contain transition metals that can be reduced to metal elements during electrolysis.\textsuperscript{44,55} These transition metals helped the growth of the tip, and the end of a CNT as TEM HAADF showed evidence of metal inside CNT and the two ends.\textsuperscript{44} Another interesting case is that Fe ions could successfully combine with produced carbon to synthesize MWCNT/Fe\textsubscript{3}C nanomaterial at 900 °C under 3.1 V with iron melt in the electrolytes.\textsuperscript{94} GeO\textsubscript{2} is another example.\textsuperscript{95} Soluble GeO\textsubscript{2} was electrochemically reduced to Ge and deposited on the cathode with carbon, and during this process, Ge anchored on the ends and the inner wall of formed carbon to grow carbon nanotubes. Considering Chen’s proposed theories about how additives’ solubility affects reaction mechanisms using CaO and BaO, the key
factor for CNTs formation may depend on the solubility of additives in electrolytes. Overall, one possible theory is that metal oxide additives are reduced to metal and then serve as the active sites for the formation of carbon nanotubes or nanofibers.44,55,92,94,95

In addition to metal, oxygen ions in these additives need to be examined since they play a significant role in the splitting reaction and regulate the rates of many reactions, such as the evolution of oxygen on the anode surface and the conversion of CO2 to CO32−. Therefore, there exists an optimal quantity of additives that should be applied to each system. Metal oxides are crucial for supplying oxygen ions when molten chlorides are applied as electrolytes. There is no carbon deposition detected in the absence of metal oxide additives.78 The metal oxide additives enable not only to capture CO2 and to initiate the subsequent carbon deposition but also to introduce significant defects into final carbon products (e.g. CNT).41,80,81 The introduction of over-dosed O2− has a drawback on CNTs formation. 30 wt% BaO with 0.04 wt% Fe2O3 and 0.04 wt% Cr2O3 additives led to 20% CNTs yield, which was about 10% higher than 7.1 wt% BaO but 60% less than using 0.1 wt% of Fe2O3. Deng reported that the CaO additive was solidified and covered the cathode when O2− was over-dosed.81 As shown in eqn (1), the electrolysis of carbonate ions produces 3 units of oxide ions. These oxide ions near the cathode can easily bond with metal cations to form metal oxides. Solidified CaO showed poor CO2 absorption, and the covered cathode lost activity. Moyer et al. also reported that Li2O build-up at the cathode lowered the reaction and decreased the carbon graphitization degree.86 Gao’s article provides another explanation that external O2− from dissolved oxide additives lowers the O2− concentration gradient in the electrolyte, and thus it slows the diffusion and limits the electrolysis rate.64 Additional research must be conducted to fully comprehend.

Therefore, researchers also attempted to manage oxygen ion products and continuously remove them instead of increasing oxygen ions in the system to capture CO2. Yet LiBO2 has been reported to be an effective additive. BO2− acts as an O2− absorbent and converts into BO33−, which later reacts with CO2 to produce CO32− and BO2−.57 The CO2 concentration was reduced from 14% to 7%. The LiBO2 free electrolytes presented a CO2 concentration drop of 2.1%, only one-third of the concentration drop in LiBO2 electrolyte.57 The reduction potential was reduced by 400 mV in this attempt, which resulted in a lower applied voltage at the same current density and a 60% reduction in energy consumption.

2.3 Electrodes

The two crucial elements in this electrolysis system are the anode and cathode, which are responsible for oxygen evolution and carbon deposits, respectively. Therefore, the anode must promote oxygen generation, while the cathode should have active areas for particular carbon nanostructures. Both electrodes nonetheless share some characteristics in common, such as resistance to corrosion in hostile situations with molten salts.

Through the CO2 splitting reaction, the changes on electrodes cause current fluctuation and unstable performance; thus, it is important to avoid corrosion due to molten salts or oxygen evolution effects on electrodes. Corrosion of carbonates can even dissolve the alumina or zirconia container.72 Corrosion easily alters electrode surface and compositions. When the effective anode area significantly decreases, the current density can have a 66% drop.67 While formed carbon expanded on the cathode surface, the current density increased.81 Even when the used Ni electrode seemed unchanged, as observed by eyes, the green residue in the electrolyte indicated part of Ni was oxidized and escaped.96 More stable metals, alloys or oxides should be utilized to minimize corrosion, such as NiCr alloy and TiO2.

2.3.1 Cathode. Metals, alloys, metal oxides, and carbon-based materials are the different categories of cathode materials. Among these, metals are the favourite choice as it is believed that metal particles decide carbon nanostructure types based on density functional theory.57 Fig. 8 illustrates how cathode materials determine the composition of the final carbon products. A metallic component in the cathode can be reduced to metal particles in the system. Nanoscale metallic impurities found in the carbon framework indicate that metal works as a catalyst in the system.98 Based on this mechanism, cathode material can be engineered to insert specific metallic layers in the formed carbon products. For example, Cr–O can be inserted to form a Cr–O–C interlayer at 700 °C under 2.8 V.99 But the metal selection is limited to the ones that do not have a strong catalysing effect on the Boudouard reaction.72 In general, Fe, Ni, Ti, Mo, Pt, their metal oxides, and alloys are widely used as the cathode in molten salt CO2 capture.

Iron is earth-abundant, affordable metal and has incredible influences on carbon products. During electrolysis, a stainless steel cathode releases Fe and other alloying metals, including Ni and Cu.100 These ions result in a micro explosion and help form graphene when CO is produced. Douglas’s research group manipulated the CNTs sizes by adjusting Fe sizes, as shown in Fig. 9.101

In addition to Fe, a copper cathode enhances the formation of a unique ball structure of graphene, while a nickel cathode leads to flat graphene sheets. The various carbon nanostructures indicate the active metal atoms on the cathode act as the nucleation sites and catalyse the development of carbon films.100 Ti is another suitable material as Ti is chemically stable in molten salts, and the formed oxide layer, TiO2 or Li2TiO3, is also conductive and insoluble up to 900 °C in Li2CO3 and Li2O.72 Zn is another case of how cathode metal alters carbon nanostructures. Zn galvanized steel cathode surface generates a high percentage (over 80%) of carbon nanofibers, which cannot be achieved by using 316 stain steel cathode.92 One way to explain these
Experimental observations can be through the density functional theory.\(^9^7\) It showed that the π–d bond between the metal particles and nanotubes encouraged the nanotube growth, and the overlap of the d orbitals from Zn and Ni could improve the nanotube quality.\(^9^7\) However, the interaction of oxygen ions and metals was not considered, including the formation of metal oxides and the solubility of metals and metal oxides.

Graphite is not a good cathode choice as it quickly swells and decomposes due to electrolyte metal intercalation, even under a low cathode current of 30 mA cm\(^{-2}\).\(^7^2\) Additionally, the CV scanning results showed that carbon triple bonds were electrochemically converted into carbon, which is more difficult on graphite than metals such as Ni.\(^1^0^2\)

### 2.3.2 Anode

\(O^2^-\) ions diffuse through the molten salt and accumulate on the anode to produce oxygen gas. \(O_2\) concentration was measured to increase by about 10 mol% comparing the effluent gas before and during electrolysis, as presented in Fig. 10(b).\(^7^2\) The anode is responsible for catalysing oxygen generation and avoiding accumulating \(O^2^-\). Removing \(O^2^-\) timely from the molten salts ensures the required electrical current for carbon deposition.\(^6^7\) As \(O^2^-\) ions do not exist freely in the electrolyte; they bond with carbon dioxide or metal ions to form carbonate ions and metal oxides. It is commonly believed that the diffusion of oxygen ions (or carbonates ions and metal oxides) is the rate-determining step.\(^5^7,^6^4,^6^5,^8^1\) Because of the unique sluggish diffusion, the concentration of outlet oxygen gradually decreased.

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**Fig. 9** Schematic illustrations: (a) electrolysis setup, (b) catalyst of varying thickness and growth time controlling the CNT diameters, (c) catalyst-coated stainless-steel cathode before, (d) after 60 min growth of CNTs.\(^1^0^1\)

**Fig. 10** (a) Digital photos of Ni, Ni\(_{10}\)Cu\(_{11}\)Fe and SnO\(_2\) electrodes before and after serving as the anode; (b) gas chromatograms of the outlet gas before and during electrolysis using the SnO\(_2\) anode.\(^3^5\)
increase over electrolysis time. At the same time, the materials should also be robust enough to resist oxidation in the long run. Anode material can also be classified into metals, alloys, metal oxides, and carbon materials. The common materials are Pt, Ni, NiO, Ni-based alloy, and SnO2. Developing suitable anode materials has always been a significant challenge and research hotspot, especially when the effectivity of cathode materials is controversial due to carbon deposition.

Metals own satisfying conductivity, but their poor durability seriously limits their applications. The anodic dissolution order of metals in molten CaCl2−CaO was Fe, Cu, Co, Ag, Ni, Mo, and Pt, shown in Fig. 11. A higher polarization current density at a potential indicates the dissolution of such metal is faster. Thus, Pt has outstanding stability among all these pure metals. Pt’s superior durability was proved again in the anodic polarization curve in molten Li2CO3−Na2CO3−K2CO3. However, the high price of this noble metal hinders its real-world application.

Metal oxides were investigated as anode materials, targeting high corrosion resistance and lower prices compared to Pt. Ni is of great interest to scientists because it naturally generates a NiO top surface layer with more resistance. Fig. 11(b) shows NiO could have comparable resistivity to Pt. Other Ni-containing materials, such as (1−x)CaTiO3−xNi, have been studied. Among them, 0.5CaTiO3−0.3Ni and 0.4CaTiO3−0.6Ni materials present satisfying anodic and stable performance with a corrosion rate of 4.958 × 10−7 g cm−2 h−1. However, Du et al. pointed out that temperature played an important role in influencing the formation of a Ni oxidized layer on the Ni anode. At a temperature lower than 575 °C, Li2Ni1−xO was the main oxidation product, which is soluble in the carbonate electrolytes. Only at temperatures above 575 °C could an evenly distributed, insoluble, and robust NiO layer form, which could shield the anode from further oxidation.

Other metal oxides also show a positive possibility of being applied as an anode, including SnO2, RuO2−TiO2, and TiO2. Among the mentioned metal oxides, the SnO2 anode shows similar polarization curves compared to Pt and Ir and becomes a popular anode choice. Fig. 10(a) presents the photos of a SnO2 electrode before and after the electrolysis, where no obvious mass loss is observed. In an extreme case of 500 hours electrolysis, the SnO2 anode lost less than 0.1 wt%. However, the polarization curve slopes of SnO2 are less significant than those of Pt and Ir, indicating the oxide has a worse oxygen evolution activity on SnO2. RuO2−TiO2 was employed in molten chlorides, and there were no physical changes observed after a 4 hour operation. But Ru is also a noble metal on Earth, and Ti oxides lack stability compared to other oxides. Additionally, there is a lack of records for RuO2−TiO2 performances in molten carbonates.

Alloys can also be promising anode materials thanks to their satisfying properties. Compared to metal oxides, alloys have better conductivity and malleability; alloys also show better corrosion resistance compared to pure metals. Ni-based alloys are the most popular anodes used in carbonate electrolytes. Ni alloy can have two roles based on different metal atoms: a NiO layer as a protective layer is formed during the electrolysis. In contrast, other metal particles in the alloy are believed to catalyse different carbon nanostructures. Ni10Cu11Fe is one example of this alloy strategy. By observing with eyes, the oxidized layer of NiO occurred on the anode surface due to the specific green colour of NiO, different from other oxides or metals, but there was no dimension change of the anode observed after over 100 hours electrolysis. Another case for Ni alloy is Ni−Cr alloy, where NiO is still the leading protective layer against corrosion. Cr2O3, the oxide form of Cr in the alloy, cannot be detected, which again indicates NiO acts as the protective layer and remains during the electrolysis. Besides the protective surface strategies, other types of alloys are applied to investigate the effects of metal particles on carbon nanostructures. Fe materials were also tested previously for anode performances. Incoloy, an Iron-based alloy with over 40% iron content, released Fe ions into the system when it was used as an anode. Because the iron content is large in Incoloy, the released Fe ion amount was significant, which combined with carbon and formed iron carbide on the CNTs external walls, resulting in a magnetic carbon material.
In some cases, a solid electrolyte is utilized as an anode to act as an oxygen ion conductor. ZrO$_2$ was expected to fasten oxygen evolution. The anode contains a ZrO$_2$ tube filled with carbon power to enhance electrical conductivity, and a stain steel pipe inserts in the carbon power and connects to a power supply. However, the experimental results were far from satisfying. The conductive carbon diffused in the ZrO$_2$ lattice and reacted with oxygen to reproduce CO$_2$. Thus, the reason for unsatisfying CO$_2$ conversion could be the technical design of the anode.

It is also worth mentioning that simply increasing the anode surface largely helped the oxygen ion mass transfer, reduced oxide build-up on the cathode surface, and controlled CNTs size, as shown in Fig. 12. Notably, the ratio of 20:1 was not favoured for CNTs growth, which can be explained by the dramatic area difference between the electrodes. The noteworthy difference resulted in a mismatched electric field, leading to low current efficiency.

### 2.4 Temperature

Temperature plays a critical role in electrolytic processes, product compositions, and material structures of produced carbon. For example, CNTs are more likely to form at operation temperatures lower than 700 °C, while CNS or CO favours higher temperatures. Fig. 5 describes how temperatures and voltages affect the reactions. Under the same potential, different reactions are thermodynamically favourable at different temperatures.

Temperature easily changes electrolyte properties, which later affects CO$_2$ absorption and conversion. Increasing temperature leads to a reduction in the stability of carbonates and CO$_2$ solubility. Increasing temperatures shift the decomposition equilibrium towards the product side, producing more metal oxides and CO$_2$. The CO$_2$ volumetric mass transfer coefficients in carbonates decreased with increasing temperature, which negatively influences CO$_2$ physical dissolution. The formation of CO$_3^{2-}$ in eqn (3), is also weakened with increasing temperatures. For carbonates, it is even worse as heat decomposition results in related instability and then decreases CO$_2$ solubility with increasing temperatures. In addition, the diffusion rate of carbonate ions directly corresponds to temperatures, which obeyed Arrhenius’ Law. An experimental data sample is shown in Table 5. Based on the data and Arrhenius’ Law, the activation energy is calculated to be 35.8 kJ mol$^{-1}$. It is also revealed that temperature effects on CO$_3^{2-}$ diffusion are relatively small.

The increased temperature can bring some negative effects to the electrolysis. The electrical resistance of electrolytes typically decreases as temperature increases. For example, the current increased by 500 mA from 550 °C to 650 °C, and carbon layers were produced faster and thicker as the kinetics and diffusion rate increased.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>D x 10^5 (cm^2 s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>973</td>
<td>4.46</td>
</tr>
<tr>
<td>993</td>
<td>4.62</td>
</tr>
<tr>
<td>1023</td>
<td>5.31</td>
</tr>
<tr>
<td>1043</td>
<td>5.90</td>
</tr>
<tr>
<td>1063</td>
<td>6.54</td>
</tr>
</tbody>
</table>
researchers pointed out that lower salt resistance did not necessarily mean higher current efficiency (Table 6). The maximum current efficiency remains stable under varying temperatures but varies at different voltages. Thus, the optimal operation conditions require further investigation to determine.

Monitoring temperature can help achieve the desired structure and composition of carbon products. With the same operating conditions except for temperatures, a honeycomb structure of carbon was observed at 577 °C, but nanotubular carbon was obtained at an elevated temperature above 600 °C. Another similar case was the carbon nanostructures changed under 2.6 V, and temperature varied from 650 °C to 850 °C. At 650 °C, the produced carbon was thick graphite. With the temperature increasing to 750 °C, flat graphite sheets with graphene were observed. A further increase in temperature to 850 °C resulted in flatter sheets of graphene with fewer layers. An increasing temperature also encourages the development of CNTs and suppresses the growth of CNS when transition metals, such as Ni, Cr, and Fe, are used as catalysts.

As shown in Table 7, combustion activation energy decreased with increasing operation temperature under the same voltage supply. As the energy barrier decreases with higher temperature, it is easier for carbon to deposit on the cathode, which matches the increased deposition rate in Table 6. This lower energy barrier could also explain why smaller carbon particle sizes were obtained. From Table 8, it is seen that increasing operating temperatures resulted in higher carbon contents and lower O, Fe, and K contents, except for Cr. Higher voltage and temperature surprisingly had a passivation effect on the anode, reducing Cr and Fe contents in the carbon.

Not only the electrolysis temperature but the drying temperature following the washing could change the composition of the products. Washed carbon samples were dried at 80, 400, and 1000 °C, and it is reported that carbon nanoparticles at 400 °C contained the highest surface area detected by BET and the largest Li and Na capacity amounts, providing superior electrochemical performances. It is also found that the in-plane layer stacking dimension decreases gradually from 74 nm at 80 °C to 29 nm at 1000 °C.

### 2.5 Voltage & energy efficiency

The voltage of the system has an impact on the contents and the morphology of the products. As shown in Fig. 5, voltage is as important as temperature, and both play a significant role in determining the electrolysis reaction. However, a higher voltage supply also indicates large energy consumption. Considering the energy costs, the balance of product quality and operation settings needs to be carefully maintained to achieve the optimum profit. Additionally, the voltage should be carefully balanced: sufficient current enlarges carbon deposition rate while higher current results in a strong electric field and leads to difficult carbonate anion diffusion towards the cathode; Table 6 shows a decrease in deposition rate when the voltage increased from 4 to 5 V at 540 °C. The behaviour can be explained by the formation of CO2, but the influence of the electric field on the diffusion of carbonate ions has not been investigated.

The electrolysis voltage should vary depending on the electrolyte cations and the amount of energy needed to split carbonates at a particular temperature. To minimize impurities in carbon products, the voltage, in general, should be less than the theoretical deposition potential of alkali cations or chlorine evolution of electrolytes. Taking Li2CO3 electrolyte as an example, the applied voltage should be

### Table 6 Estimated carbon deposition rates and current efficiencies during electrolysis in molten Li2CO3-K2CO3 at various temperatures and voltages

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Deposition rate (g cm² h⁻¹)</th>
<th>Current efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>540</td>
<td>1.0</td>
<td>0.0306</td>
<td>91</td>
</tr>
<tr>
<td>3</td>
<td>593</td>
<td>1.0</td>
<td>0.0306</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>1.0</td>
<td>0.0613</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>540</td>
<td>1.0</td>
<td>0.0917</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>593</td>
<td>1.0</td>
<td>0.0851</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>700</td>
<td>1.0</td>
<td>0.0488</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>540</td>
<td>1.0</td>
<td>0.0712</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>593</td>
<td>1.0</td>
<td>0.0665</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>700</td>
<td>1.0</td>
<td>0.0248</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>540</td>
<td>0.5</td>
<td>0.1107</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>593</td>
<td>0.5</td>
<td>0.0874</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td>700</td>
<td>0.5</td>
<td>0.0400</td>
<td>73</td>
</tr>
</tbody>
</table>

### Table 8 Elemental composition of carbon deposited after 1 h electrolysis in Li2CO3-K2CO3 at (a) 593 °C and different cell voltages, and (b) 4.0 V and different molten salt temperatures

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>(a) Cell voltage</th>
<th>(b) Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (K)</td>
<td>83.39</td>
<td>85.20</td>
<td>88.54</td>
</tr>
<tr>
<td>O (K)</td>
<td>12.80</td>
<td>13.85</td>
<td>10.71</td>
</tr>
<tr>
<td>K (K)</td>
<td>0.55</td>
<td>0.28</td>
<td>0.45</td>
</tr>
<tr>
<td>Cr (K)</td>
<td>1.20</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Fe (K)</td>
<td>2.07</td>
<td>0.68</td>
<td>0.47</td>
</tr>
<tr>
<td>C (K)</td>
<td>83.56</td>
<td>85.20</td>
<td>92.33</td>
</tr>
<tr>
<td>O (K)</td>
<td>13.46</td>
<td>13.85</td>
<td>5.65</td>
</tr>
<tr>
<td>K (K)</td>
<td>1.12</td>
<td>0.28</td>
<td>1.73</td>
</tr>
<tr>
<td>Cr (K)</td>
<td>0.79</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Fe (K)</td>
<td>1.83</td>
<td>0.68</td>
<td>0.28</td>
</tr>
</tbody>
</table>

---

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controlled between −2.964 and −1.719 V at 600 °C to produce carbon and avoid Li formation using data from Table 4. However, this range is not mandatory in practice, which means the voltage setting can exceed the potential of alkali metal formation. Numerous research studies were conducted under much higher voltage. It is believed that, under an operating voltage higher than alkali deposition potential, the deposited alkali metal particles can act as nucleation sites and encourage the growth of unique nanostructures. Ge, Ni, Fe, and other metals were observed in SEM or TEM to grow nanowires by serving as two ends of the tube structure.44,95

Similar to how they can be modified by temperature, the compositions and architectures of the products can also be altered by voltage. It is common knowledge that at a current between 0–2 A cm−2, CO2 converts into carbon, and no gas is generated at the cathode, while a higher current can lead to the formation of CO gas.106 With the extremely large current of 33 A, nano-diamonds could be produced at low pressure at 800 °C.109 At 2.8 V, the carbon product appears to be a carbon film. When the voltage increases to 4.0 V, the carbon presents a flocculent exterior.35 Carbon, as well as alkaline metal depositions, decide the final nanostructures of formed carbon, especially at a high cell voltage (over 5 V).71 The SEM images of the carbon obtained at different voltages are shown in Fig. 14. As shown in Table 9, the specific surface area of carbon increases with increasing voltages. Similar results are also observed in Ijije’s article.73 The particle sizes of carbon become smaller with rising current densities.91 However, the crystallinity of carbon does not change with voltage. Kaplan and his colleagues operated the experiments under −1.6, −2.4, and −6.0 V remaining other parameters the same.108 From Kaplan’s data, the crystallinity of carbon products was similar but slightly reduced when the voltage became more negative. Along with more negative voltage, the side reactions play a more important role. The carbon samples grow more impurities, including oxygen and lithium.108 The weight percentage changes aligned with the theories of alkali metal deposition are expressed in eqn (6). Mesopores increase with elevated voltage.73 Additionally, a combination of high and low current densities in the process can lead to different carbon nanostructures. For instance, amorphous carbon is obtained if the current density is kept at 100 mA cm−2 for the cathode throughout the process. While CNF is formed when the current density is set low initially, e.g., 5 mA cm−2 for 1 h, and gradually increases to 100 mA cm−2 and remains at this density.72 Ren et al. suggested the difference in carbon nanostructure is caused by the anode metal deposition at low current density, such as Ni, which is critical for CNF nucleation formation.92

The activity of oxygen ions is also affected by voltages. Fig. 13 shows the Chrono-potentiometric plots for the anodic oxidation of carbon. The rapid increase in the current between the second and third plateaus demonstrates the activity of oxygen ions in the molten salt is slower than the activity of CO3−. The CVs Ijije and his team obtained show there was no clear signal of anodic discharge of the O2− ions, which also indicates the amount of O2− ions generating O2 is less than the amount of O2− ions produced by carbonate ion splitting.41 The loss of oxygen ions can be explained by eqn (3), where the O2− ions absorb carbon dioxide and form carbonate ions. However, how different voltages influence the O2− transfer and oxygen generation has not been fully reported yet.

The required voltage is directly associated with current efficiency and energy consumption. Although high voltage may result in a desirable morphology of carbon product, the energy penalty might overweight the improvement. Fig. 15 shows the highest temperature or voltage is not the optimal condition for reaction efficiency or energy consumption. Temperature and voltage should be selected for best efficiency, preferred carbon structure, and affordable energy consumption. Harsh operation conditions are always accompanied by excessive energy consumption. Tang’s research results demonstrate the lowest energy consumption was around 38 kW h kg−1 CO2 at 3 V and 550 °C, which aligned with Yin’s finding.35,71 It should be emphasised that their calculations of energy consumption did not account for the heat needed to maintain high temperatures. Lack of heat consumption could result in mistakes when determining the best operating conditions because temperatures and voltages both affect how quickly carbon is deposited. Most importantly, more research should be conducted in the future to determine how voltage affects carbon deposition rate and its nanostructures.

2.6 Composition of inlet gas

Power plant flue gas usually contains various gas components, and their compositions are changed with combustion conditions.109,111 CO2, O2, SO2, NOx, and vapour are commonly identified in the flue gas. Molten salt electrolysis has been performed under various CO2
concentrations, ranging from 0.04% (atmospheric concentration), 14% (typical CO\textsubscript{2} concentration in the flue gas), to 100%\textsuperscript{35,57,92}. It is unnecessary to concentrate CO\textsubscript{2} prior to electrolysis. It was reported that half of the CO\textsubscript{2} can be absorbed from gas with 14% CO\textsubscript{2} and converted into carbon with 90% current efficiency\textsuperscript{57}. Even for 0.04% carbon dioxide concentration, the concentration step is not required, and current efficiency can still be near 100%\textsuperscript{92}.

However, other gas impurities’ effects have not been fully reported. Investigating how these impurities affect the electrolysis reaction and products is required before applying this electrolysis approach to commercial post-combustion plants. N\textsubscript{2}, as an inert gas, is often used as the carrier gas for flow rate and pressure modifications. However, O\textsubscript{2}-related effects have not yet been fully observed. The influence of vapour was carried out using LiOH additives as an alternative because of the difficulty in the quantification of vapour added to the system\textsuperscript{48}. Under a typical operating condition of molten salt electrolysis, vapour has a good chance of undergoing the water-splitting reaction, which expects to have a significant impact on the electrolytic process\textsuperscript{47,48,112}.

Shown in Table 10, H\textsubscript{2} is the major product, over 50% in all cases, when CO\textsubscript{2} is fed into molten carbonates with LiOH additives. With appropriate conditions, the current efficiency for syngas could achieve 90%\textsuperscript{112}. Ji’s report shows similar results that an increase of 0.5 V significantly promoted CO formation and resulted in 33.6% CO and 64.2% H\textsubscript{2} in the gas products\textsuperscript{48}.

SO\textsubscript{2} in the flue gas undergoes electrolysis in the molten carbonate salt with Li\textsubscript{2}SO\textsubscript{4} additive. Similar to CO\textsubscript{2}, SO\textsubscript{2} can react with O\textsuperscript{2-} and form Li\textsubscript{2}SO\textsubscript{4}, which is later reduced into sulfides or sulphur. The resulting sulphur is inserted into deposited carbon nanostructures, forming sulphur-doped carbon\textsuperscript{79}. Instead of accumulating in molten salts, it is observed that sulphur element was found at the gas outlet of the cathode\textsuperscript{113}. Sulphur contents in the system can also react with carbon to form CS\textsubscript{2}, which is helpful in removing imperfect carbon and leads to graphitization over 500 °C. It suggests that the deposited S and S\textsuperscript{2-} also contribute to the low-temperature graphitization\textsuperscript{114}. In the end, sulphur contents in the feed stream can be completely captured\textsuperscript{34}.

Eqn (14) and (15) are the two possible reactions happening in Li carbonate molten salts\textsuperscript{113}. Li\textsubscript{2}SO\textsubscript{4} has lower decomposition potentials compared to Li\textsubscript{2}CO\textsubscript{3}, so the sulphur reduction current is limited by diffusion\textsuperscript{113}. CO\textsubscript{2} can still be converted into carbon or CO, but with reduced efficiency; for example, the CO production faradaic efficiency with SO\textsubscript{2} inlet is reduced to 54%, as shown\textsuperscript{113}.

\begin{equation}
4\text{Li}_2\text{CO}_3 + 4\text{SO}_2 \rightarrow \text{Li}_2\text{SO}_4 + \text{Li}_2\text{S} + 4\text{CO}_2
\end{equation}

Table 9 BET surface area (m\textsuperscript{2} g\textsuperscript{-1}) of the carbon powders prepared under different conditions\textsuperscript{71}

<table>
<thead>
<tr>
<th>Conditions</th>
<th>3.5 V</th>
<th>3.0 V</th>
<th>4.0 V</th>
<th>4.5 V</th>
<th>5.0 V</th>
<th>5.5 V</th>
<th>6.0 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>450 °C</td>
<td>306.76</td>
<td>558.10</td>
<td>536.41</td>
<td>613.76</td>
<td>526.60</td>
<td>868.31</td>
<td>856.26</td>
</tr>
<tr>
<td>550 °C</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>212.39</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>650 °C</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>101.89</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
The Gibbs free energies show both reactions are thermodynamically feasible, but the SO₂ absorption rate of melts is slower than the reaction. If oxygen is also fed into the system and the volume ratio of SO₂ to O₂ is less than 2, SO₂ can be consumed rapidly through the following reactions shown in eqn (16) and (17).

\[
\begin{align*}
2\text{Li}_2\text{CO}_3 + 2\text{SO}_2 + \text{O}_2 & \rightarrow 2\text{Li}_2\text{SO}_4 + 2\text{CO}_2 \\
2\text{Li}_2\text{O} + 2\text{SO}_2 + \text{O}_2 & \rightarrow 2\text{Li}_2\text{SO}_4
\end{align*}
\]

Inlet gas flow rate and CO₂ concentration are additional parameters that can be tuned to suit CO formation. As shown in Fig. 16(a), the conversion of CO₂ to CO increases with rising flow rates, but the increase reaches a plateau at a certain flow rate. The high gas flow rate improves the mixing of gas and molten salts and the dispersion of ions. But due to the low residence time of CO₂, complete carbon deposition cannot be reached, and the formation of CO is favoured in this case. However, CO formation can be suppressed by further increasing gas flow rates. Overall, a 2-electron cathodic reaction is favoured in this case to form CO gas.

Fig. 16(b) provides the ratio of CO₂ concentration to its CO product. When CO₂ concentration increased from 5% to 15%, CO concentration correspondingly jumped from 0 to 90%.

Table 10 Gaseous products detected at the exit of a molten salt cell with Li₁.₄₃Na₀.₂K₀.₂CO₃ salt and 10 wt% LiOH additive

<table>
<thead>
<tr>
<th>No.</th>
<th>Electrolysis parameters</th>
<th>Gas content</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Voltage (V)</td>
<td>CH₄ (%)</td>
<td>CO (%)</td>
<td>H₂ (%)</td>
</tr>
<tr>
<td>1</td>
<td>450</td>
<td>2.0</td>
<td>18.2</td>
<td>—</td>
<td>81.7</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
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<td>22.1</td>
<td>—</td>
<td>78.6</td>
</tr>
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<td>3</td>
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<td>40.1</td>
<td>—</td>
<td>59.5</td>
</tr>
<tr>
<td>4</td>
<td>600</td>
<td>2.0</td>
<td>30.4</td>
<td>0.1</td>
<td>69.3</td>
</tr>
<tr>
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<td>650</td>
<td>2.0</td>
<td>27.3</td>
<td>2.4</td>
<td>70.9</td>
</tr>
<tr>
<td>6</td>
<td>550</td>
<td>1.0</td>
<td>—</td>
<td>—</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
<td>550</td>
<td>1.5</td>
<td>—</td>
<td>—</td>
<td>100</td>
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<tr>
<td>8</td>
<td>550</td>
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<td>13.3</td>
<td>9.2</td>
<td>77.2</td>
</tr>
<tr>
<td>9</td>
<td>550</td>
<td>3.0</td>
<td>5.4</td>
<td>20.2</td>
<td>74.0</td>
</tr>
<tr>
<td>10</td>
<td>550</td>
<td>3.5</td>
<td>1.9</td>
<td>33.6</td>
<td>64.2</td>
</tr>
</tbody>
</table>

3 Conclusion & future challenges

Molten salt CO₂ electrolysis is an innovative CO₂ capture and conversion method targeting power plant flue gas to achieve CO₂ zero emission. This molten salt system presents multiple advantages, including high current efficiency, simpler solid separation of produced carbon, engineered carbon nanostructures, and positive cash flow. Carbonates hold better CO₂ absorption ability and higher current efficiency compared to chlorides as electrolytes. Considering metal deposition side reactions and melting points, lithium, sodium, and potassium carbonates are widely used and combined. Oxide additives are favoured to increase gas sorption, especially in chlorides, and also impact carbon nanostructures. The cathode is another factor influencing carbon nanostructures, and popular choices are Fe, Ni, Pt, their metal oxides, and alloys. Anode is responsible for the critical oxygen evolution so the materials should have a strong durability and anti-corrosion ability, such as metal oxides and alloys. Temperature and voltages are the two significant parameters in this electrolysis, as they control the activation energy of the electrolysis. Higher temperature suppresses carbon formation but improves CO production. The study of voltage focuses on not only the electrolysis potentials but also the energy consumption for optimal efficiency.

However, molten salt CO₂ electrolysis leaves some research gaps. The first challenge is scaling up and corrosion’s effects on the equipment. To date, all the research results are produced from a lab-scaled system, and there has not been a commercial-scaled system yet. The mass and energy balance, energy efficiency, cost of materials, the activity of electrocatalysts, waste heat utilization, and system designs are unknown or obscure engineering aspects. There exist obstacles in maintaining a continuous operation, recovering salts, and removing carbon that has grown on the cathode. Although Licht’s research team did suggest a method for separating salt electrolytes, some problems still appear to prevent the commercialization of electrolysis. These problems include the energy loss associated with preheating the separation device to 750 °C, carbon build-up on the cathode surface, and potential device corrosion. For the recovery process and saving acid from dissolving carbonates in current lab-
scale experiments, a molten CaCl$_2$ dissolver was proposed to extract carbon from CaO and CaCO$_3$, which are insoluble in water. But the corrosion tests of this method should be obtained to compare the influence of CaCl$_2$ and other soluble carbonates. Furthermore, equipment and electrodes can corrode rapidly due to high temperatures and the corrosive nature of molten salts under general electrolysis operations. More research is therefore needed to develop reliable electrodes that are more affordable, perform better, and balance absorption kinetics and reaction mechanisms. To enhance CO$_2$ conversion efficiency, the shape and surface area of electrodes should be investigated.

The formation of uniform carbon nanostructures can be another challenge. Morphology of carbon products is sensitive to operating conditions; for example, MWCNTs took up 40 vol% of Novoselova’s cathode sample and about 80% CNFs in Ren’s results. In the latest report, the highest percentage of a specific nanostructure was 98%. A 100% uniform carbon nanostructure has not been obtained. In addition to the carbon nanostructure, it is important to investigate the carbon deposition rate with different additives. Furthermore, these reports made no comment on the factors that affect the rate of carbon deposition or the effectiveness of CO$_2$ capture; hence, further research is necessary to close this knowledge gap.

More fundamental research is required to fully understand the electrolysis reaction mechanisms, such as quantifying oxides and carbonate ion concentration changes and their mass transfer. Although the operating parameters and their effects on electrolysis performances and products have been investigated, there are still some challenges, such as quantifying rate-determining step and monitoring oxygen ion mass transfer during electrolysis and CO$_2$ absorption. The influences of the electric field on carbonate anions should also be examined to study the diffusion mechanism of carbonate anions towards the cathode. The density functional theory (DFT) has been employed to interpret the fundamentals of metal particles as nucleation sites for the formation of nano carbon products. 

Experimental validations are essentially expected. More DFT research and calculation should be performed to provide a more comprehensive study of different parameters and conditions at the molecular level. There also lacks records for a full analysis of the effects of flue gas impurities, especially for NO$_x$, water vapour, and oxygen. Besides its compositions, the conditions of the flue gas, including pressure and temperature, have not been well studied. Other fundamental knowledge deserves attention, including electrode/electrolyte interface analysis, mass transfer between gaseous CO$_2$, liquid electrolytes, and solid electrodes, reactants’ influences on electrolysis, CO$_2$/electrolyte fluid dynamics, and more. Other basic analysis, such as safety and economy analysis, is also missing in this field.

**Conflicts of interest**

The authors declare no conflict of interest.

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