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Capture and electrochemical conversion of CO₂ in molten alkali metal borate–carbonate blends†

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A family of blended compositions of molten mixed lithium and sodium borate (Li_{1.5}Na_{1.5}BO₃) and eutectic lithium–potassium carbonate (Li_{1.24}K_{0.76}CO₃) salts has been introduced as reversible carbon dioxide absorbents and as media for CO₂ electrolysis for carbon conversion. Material properties, temperature effects and kinetics of CO₂ uptake were examined. Li, Na borate can absorb up to 7.3 mmol g⁻¹ CO₂ at 600 °C. The blended borate–carbonate compositions are molten in the 550–600 °C temperature range, with viscosity adjustable to within a 10–1000 Pa s window depending on the borate/carbonate ratio. The blends can withstand cyclic temperature and CO₂ pressure swings without significant deterioration of their CO₂ uptake capabilities. Addition of eutectic carbonate into mixed Li, Na borate salts lowers overall CO₂ uptake due to the lower solubility of CO₂ in carbonate. However, addition of the eutectic lowers the temperature of the pressure swing operation and dramatically accelerates the CO₂ uptake during the initial stage of the absorption, potentially enabling a faster cycling. Electroreduction of CO₂ and carbon deposition on a galvanized steel cathode was more effective with increasing carbonate fraction in the molten alkali borate/carbonate blend. Blended borate/carbonate compositions with 50–60% borate content possessed sufficiently high loading capacity for CO₂ and simultaneously enabled maximum carbon product yield and Coulombic efficiency. Most of the recovered carbon product was shown to be in the form of multiwalled carbon nanotube.

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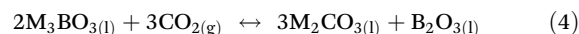
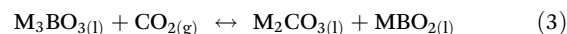
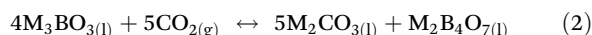
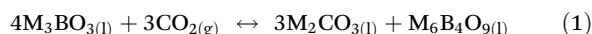
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Introduction

Efficient capture and conversion of carbon dioxide (CO₂) is a key pathway toward achieving carbon neutrality of the carbon-producing processes, which is now an imperative accepted worldwide. Among technological innovations in carbon capture, utilization and storage (CCUS) aiming at global warming relief, electrochemical capture and conversion utilizing molten salts appears to be promising.^{1–5} The potential for efficient generation of O²⁻ and CO₃²⁻ anions from CO₂ at elevated temperatures and a large operational range for electrochemical oxidation–reduction applications make molten salts an excellent medium for the CCUS processes. Thus far, only metal carbonates and chlorides (and their blends) have been used as molten salt materials with the CO₂ solubility acceptable for electrochemical conversion of CO₂.^{1,4–10}

Our group has advanced molten alkali metal borates such as lithium borate (Li₃BO₃) and mixed lithium, sodium borates

as reversible CO₂ sorbents due to their large and temperature-reversible sequestration capacity for CO₂ and acid gases, which generally exceeds the capacity of other molten salts.^{11–19} Thermoreversible reactions of the alkali metal borate glasses with CO₂ are well-documented.^{11–20} The chemisorption of CO₂ by alkali metal (M) borate M₃BO₃ results in the reversible formation of carbonate (M₂CO₃), metal oxide (M₂O)–boron oxide (B₂O₃) binary compounds, and metaborate (MBO₂) as follows.



(M = Li, Na, K, etc.).

Forward chemical reactions of CO₂ with metal borates occur primarily in the 400–650 °C temperature range and lead to carbon dioxide absorption and formation of metal carbonate salts. The temperature ranges over which carbonate salt forms depend on the metal utilized. The reverse reactions become favored at temperatures above 500–700 °C and result in metal carbonate decomposition and carbon dioxide release.

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In a concurrent study,²¹ we discovered that the alkali metal carbonates that result from the chemisorption of CO₂ by alkali metal borates (reactions (1)–(4)) could subsequently be converted to carbon by electrolysis in a specific temperature range. However, the formation and yield of carbon in the molten borate by CO₂ electrolysis are conditional upon saturation of the melt by CO₂, the formation of carbonate salts (M₂CO₃), and dissociation of these salts leading to the formation of carbonate anions, which are necessary for the electrolytic conversion of CO₂ to carbon:^{4–6,10}

Formation of carbonate ions:



Four-electron reduction of the carbonate ions to carbon on cathode:



Continuous formation of oxygen on the anode:



Although reactions (5) and (6) do occur with sodium, potassium and alkaline earth carbonates,⁹ the production of carbon in the form of CNTs by electrolysis in metal carbonate melts occurs primarily with Li⁺ present in the carbonate (Li₂CO₃) and proceeds together with the formation of oxygen and lithium oxide.



The formation of lithium oxide (8) is very important for the lithium carbonate recycling, as Li₂CO₃ is consumed by the electrolysis and needs to be continuously replenished by reaction of excess Li₂O (formed electrolysis product) with the CO₂ supplied:



However, the melting of lithium carbonate necessary for carbonate ion formation (reaction (5)) occurs at temperatures above 723 °C, whereas the decomposition of lithium carbonate and formation of lithium oxide (Li₂O) is achieved only at temperatures above 1200 °C. These high temperatures are problematic for proper operation, since the presence of Li₂O from lithium carbonate is a condition for CO₂ capture, which is necessary for the reversible mode of CO₂ capture and release using carbonate molten salts (temperature swing). Without the presence of metal oxides in the molten alkali metal carbonates, the capacity of the molten carbonates for CO₂ capture from the environment is low, and therefore, the subsequent electrolytic CO₂ conversion to the value-added carbon products is limited in scale and is inefficient. However, the direct addition of Li₂O to molten lithium carbonate is restricted, because dissolution of solid Li₂O in Li₂CO₃ only occurs at $T > 750$ °C. When Li₂O is added to Li₂CO₃ at 750 °C, Li₂CO₃ is observed to absorb CO₂ from air; at 550 °C, Li₂CO₃ or its mixture with Li₂O are present in a solid form and Li₂CO₃ will desorb CO₂ into air by decomposition at that temperature,²²

contrary to the intent of enhancing CO₂ sorption capacity. Therefore, lithium carbonates per se are inefficient as reversible CO₂ sorbents at medium temperatures (below 750 °C) and are commonly replaced by mixed Li, Na, K carbonates as molten salt media in CO₂ electrolysis.^{8,10,24,25}

On the other hand, eutectic salt compositions of lithium and sodium and/or lithium and potassium carbonates that possess lower melting temperatures (<750 °C) are well-known.^{26,27} Electrochemical carbonate ion reduction and carbon formation/deposition reactions from eutectic alkali metal carbonate melts in the 500–750 °C range have been reported to occur on metallic cathodes made of Ni, Pt, W, Ag, Mo, Al, Cu, and steel, as well as glassy carbon electrodes.²⁵ Carbon formation has been reported on steel electrodes in mixed melts such as Li₂CO₃–Na₂CO₃ (eutectic mole ratio, 52 : 48) or Li₂CO₃–K₂CO₃ blends (molar ratio, 62 : 38) in the 550–650 °C range.^{25,28} In the present work, we aimed to design molten salt compositions that could be applied as both (i) reversible CO₂ capture absorbents and (ii) media for the electroreduction of that captured CO₂ to value-added carbon nanotubes. We surmised that the addition of a eutectic alkali metal carbonate to the alkali metal borates could facilitate electrochemical reduction of CO₂ captured by the molten borates, given that both the borate and carbonate salts can melt and form homogeneous blends in the same preferential temperature range of 550–650 °C. Importantly, potentially deleterious autooxidizing and decarbonization reactions of carbonates by alkali metal metaborate and borates are known to occur in the 900–1000 °C range,^{12,29} but can be averted in the target temperature range.

Electrolytic production of carbon nanotubes using molten lithium carbonate compositions can be aided or mediated by the addition of small quantities of metaborates.^{30,31} Adding lithium metaborate (LiBO₂) into molten LiCl–Li₂CO₃ electrolyte at metaborate concentrations up to 1–2 wt% can thermodynamically change the reaction pathway, accelerating the electrolysis and enabling formation of the CO₂-derived products such as CO or CNT at lower cell voltages.^{30–32}

Albeit the mechanisms of the carbon nucleation and growth into CNT and other nanostructured materials in the CO₂ electroreduction processes occurring in alkali metal molten carbonates have been subjected to detailed studies.^{4–10,30,31} blends of alkali metal borates and carbonates have not been studied at large borates concentrations (>10%). Herein, we describe blended alkali metal borate/eutectic carbonate compositions that can be optimized specifically for the use in carbon capture, utilization and storage (CCUS) processes.

Experimental

General methods

Thermal characteristics and sorbent properties of the salts were analyzed by the weight and heat flow variations of the samples inside a thermogravimetric analyzer (TGA, Q50 or



Q600, both from TA Instruments, Inc., New Castle, DE) or using a differential scanning calorimeter (DSC, Q600 or Discovery DSC 250, TA Instruments). For DSC measurements, heating and cooling ramp scanrates of $10\text{ }^{\circ}\text{C min}^{-1}$ were applied in the temperature ranges up to $540\text{ }^{\circ}\text{C}$ (Discovery DSC 250) and up to $1200\text{ }^{\circ}\text{C}$ (Q600); DSC samples were sealed in aluminum pans (Discovery DSC 250) and the measurements were conducted in nitrogen atmosphere. TGA heating ramps were conducted on sample exposure to a flow of either 100% CO_2 or N_2 . Unless specified otherwise, the mass of sample was 5–10 mg; the gas flow rate was 60 mL min^{-1} . To calculate CO_2 uptake, the fractional weight change on exposure to CO_2 (MW 44.01) was normalized by the sample mass after final pretreatment by N_2 to obtain the CO_2 loading in mmol CO_2 per gram sorbent (Q_{CO_2} , mmol g^{-1}). Temperature ramps were carried out from 200 to $800\text{ }^{\circ}\text{C}$ at varying heating rates. Capacity was defined as certain CO_2 loading after uptake under a CO_2 flow.¹⁷ XRD patterns were obtained by using a 3rd generation Empyrean multipurpose X-ray diffractometer (Malvern PANalytical) equipped with a Cu radiation source and X-ray generator power of 4 kW (max 60 kV, 100 mA) at room temperature. Studied interval was $2\theta = 4$ to 70° and angular resolution, 0.026° . XRD scans within the temperature range from ambient to $600\text{ }^{\circ}\text{C}$ were performed in argon or CO_2 atmosphere using a PANalytical X'Pert Pro instrument with a 1.8 kW sealed X-ray tube source, a Cu target, and a vertical circle goniometer with a radius of 240 mm.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) experiments were conducted using a JEOL 2010 Advanced High Performance TEM and JEOL 5910 General Purpose SEM, respectively. Carbonaceous products collected on galvanized steel cathode obtained in the blends' electrolysis at $550\text{ }^{\circ}\text{C}$ were deposited onto TEM gold-coated grids from their suspensions in isopropyl alcohol followed by drying under vacuum. Elemental analysis was performed in an EPA-certified laboratory using inductively coupled plasma-mass spectrometry.

XPS spectra were measured using a PHI Versaprobe II XPS instrument with a scanning X-ray source and a UV lamp (Physical Electronics, Inc., Chanhassen, MN). Prior to taking XPS spectra on electrode surfaces, the original electrode wire was washed by acetone and water followed by drying; the wire that had been used in electrolysis and withdrawn from the molten salt at $550\text{ }^{\circ}\text{C}$ was equilibrated at ambient temperature and then gently washed by water and dried in air; the same electrode was then cleaned off by immersion in a 1% aqueous solution of nitric acid and sonication for 45 min. Peak assignments were performed using built-in instrument software.

Raman spectra of the purified carbonaceous products of the CO_2 electroreduction were measured using a Renishaw inVia Reflex Raman spectrometer (laser excitation wavelength, 532 nm) coupled to a confocal microscope.

ARES-G2 Rheometer with Forced Convection Oven (TA Instruments, Inc.), operating at temperatures up to $600\text{ }^{\circ}\text{C}$ was used with stainless steel parallel plate geometry (40 mm diameter, gap 0.5 mm). Series of single rate viscosity measure-

ments were conducted at 550 or $600\text{ }^{\circ}\text{C}$ at short step times and varying shear rates. Each viscosity datapoint was measured in triplicate.

Salt syntheses

Preparation of alkali metal carbonate. Lithium carbonate (Li_2CO_3 , ACS reagent, $\geq 99\%$) and potassium carbonate (K_2CO_3 , ACS reagent, $\geq 99\%$) were both obtained from Sigma Aldrich Chemical Co. Powderous blend of Li_2CO_3 (21.07 g, 0.285 mol) and K_2CO_3 (24.16 g, 0.175 mol) was ground at ambient temperature using mortar and pestle and was dried on air at $350\text{ }^{\circ}\text{C}$ for 8 h in an electric oven. Following cooling, the resulting eutectic Li, K carbonate (62 : 38 mol ratio of lithium and potassium carbonates, nominal composition, abbreviated $\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$) was again ground and kept in a sealed container prior to the use.

Preparation of alkali metal borate. Lithium hydroxide (LiOH, 98%), sodium hydroxide (NaOH, $\geq 98\%$, anhydrous), and boric acid (H_3BO_3 , 99.5%) were obtained from Sigma Aldrich Chemical Co. All water utilized was Mill-Q (Millipore) deionized water. Deionized water (30 mL) was gently added to a powderous mixture of solid LiOH (9.1 g, 0.39 mol), NaOH (15.03 g, 0.39 mol) and H_3BO_3 (15.88 g, 0.26 mol) and the resulting suspension was sonicated for 5 min following by heating at $60\text{ }^{\circ}\text{C}$ while stirring in a sealed bottle. The resulting suspension was allowed to dry at $100\text{ }^{\circ}\text{C}$ on air overnight and the resulting powder was gently ground by mortar and pestle and dried at $400\text{ }^{\circ}\text{C}$ for 4 h. Following cooling, the resulting Li, Na borate (composition, $(\text{Li}_{0.5}\text{Na}_{0.5})_x\text{B}_{1-x}\text{O}_{1.5-x}$, $x = 0.75$, abbreviated as $\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$) was again ground and kept in a sealed container prior to the use.

Preparation of blended borate/carbonate compositions. Weighed amounts of carbonate ($\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$) and borate ($\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$) were mixed with a spatula, ground by mortar and pestle for 5 min, dried on air in an electric oven for 3 days at $100\text{ }^{\circ}\text{C}$ and then kept in a sealed vial at ambient temperature prior to the use. Each blend was analyzed for water content using thermogravimetric analysis and the borate content (mol%) was then corrected due to the measured presence of hydrate (clathrate) water. The compositions of the borate-carbonate blends are listed in Table 1.

Electrolysis of CO_2 in borate/carbonate blend electrolyte

Electrolysis of CO_2 was conducted using a home-made temperature-controlled tubular glass reactor equipped with furnace,

Table 1 Compositions of preferred borate and carbonate blends. Borate: $\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$; carbonate: $\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$

Sample no.	Nominal borate content (mol%)	Borate content corrected (mol%)	Carbonate content corrected (mol%)
1	100	100.0	0.0
2	75	68.9	31.1
3	50	48.3	51.7
4	25	21.4	78.6
5	0	0.0	100.0



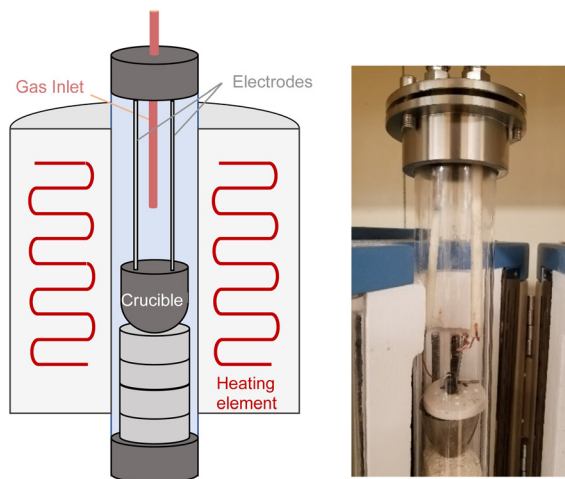


Fig. 1 Schematic and photograph of the reactor for molten salt CO₂ electrolysis.

gas inlet/outlet, stainless steel caps, and insulated electrode lines (Fig. 1). The electrode cables were connected to a computer-controlled BioLogic Model SP-101 potentiostat (Biologic, Seyssinet-Pariset, France).

The anode was a nickel crucible composed of 99.5% nickel (nominal volume, 20 mL, Sigma-Aldrich Chemical Co.). A copper coil with a copper wire lead was used as an electrical connector.

The cathode was constructed of hot-dip galvanized steel wire (Fi-Shock WC-14200, G90 coating designation according to ASTM A653; zinc coating layer thickness approximately 18 μm). The cathode was fabricated from a 14 Ga wire made into a disk with area of *ca.* 2 cm². Identical cathodes, but made of 316SS stainless steel wire (McMaster-Carr), or 99% nickel rod (Goodfellow), were used in separate series of experiments.

The details of the electrolysis experiments in this work consisted of the steps described in ESI.†

Coulombic efficiency (C_e , %) was calculated as the percent of applied, constant current charge that was converted to carbon during the CO₂ electrolysis, determined as:⁶

$$C_e (\%) = 100 \times M_{\text{exp}} / M_{\text{theor}} \quad (10)$$

where M_{exp} is the mass of purified carbon product removed from the cathode; $M_{\text{theor}} = (Q/nF) \times (12.01 \text{ g C per mol})$ is the theoretical mass, which is determined from Q , the time integrated charge passed during the electrolysis; $F = 96\,485 \text{ As mol}^{-1} \text{ e}^{-}$ is the Faraday constant, and $n = 4 \text{ e}^{-} \text{ mol}^{-1}$ is the reduction number of tetravalent carbons. The mass of carbon product M_{exp} was determined from the total mass of purified dried product multiplied by the mass fraction of total carbon in that given product sample measured by elemental analysis. Standard error for C_e was measured to be 9% in a series of independent experiments.

Results and discussion

Characterization of the molten salt properties

Our choice of the eutectic carbonate ($\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$) studied in this paper was predicated on the prior studies demonstrating relatively low melting temperature and concomitant maximum lithium content of that particular carbonate.^{26,27} High Li content can be conducive to the enhancement of carbon yield during electrolysis. On the other hand, the Li, Na borate utilized throughout ($\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$) was chosen due to the extensive prior optimization work by our group indicating that this particular composition possessed maximum CO₂ sorption capacity relative to others while maintaining liquid properties and homogeneity even after reaction with CO₂ in the molten state.¹⁷

Thermal properties of alkali metal borates and their blends with carbonates

Representative TGA and endothermal DSC thermograms on heating of samples of the studied alkali metal borate and carbonate, and their blends in a nitrogen atmosphere are shown in Fig. 2 and 3, respectively. The lithium-containing samples contained varying fractions of crystalline water. Li, K carbonate lost the majority of that water at $T > 130 \text{ }^\circ\text{C}$ and showed stability until approximately 700 °C, above which the weight loss began due to decomposition. Eutectic Li, K carbonate ($\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$) showed no further weight loss during repeated TGA cycling in the range up to 650–700 °C (data not shown).²⁸ In comparison, Li, Na borate ($\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$) appeared to be more hygroscopic than the carbonate and lost crystalline water over several stages, above 100, 230, and 400 °C. In the repeated cooling and heating cycles, the borate showed no signs of weight loss at temperatures up to at least 800 °C. The borate-carbonate blend pre-treated at 600 °C in nitrogen atmosphere lost less than 1% of its weight over a broad range of temperatures (Fig. 2). Hence, the prepared blends showed promise as

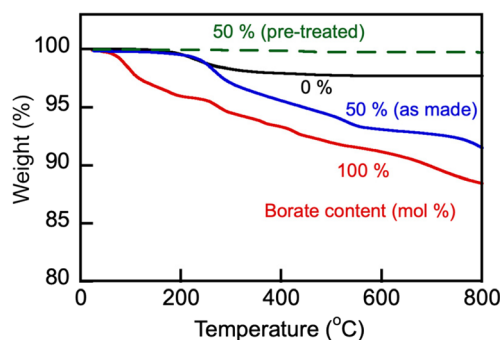


Fig. 2 TGA heating ramp (10 °C min⁻¹) of as-made carbonate ($\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$), borate ($\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$) and as-made and pre-treated blend (1:1 mol/mol, sample no. 3 in Table 1) in nitrogen atmosphere. The blend sample was pre-treated by its equilibration at 600 °C in N₂ atmosphere for 1 h. Numbers stand for nominal initial content of borate (mol%) in the samples.



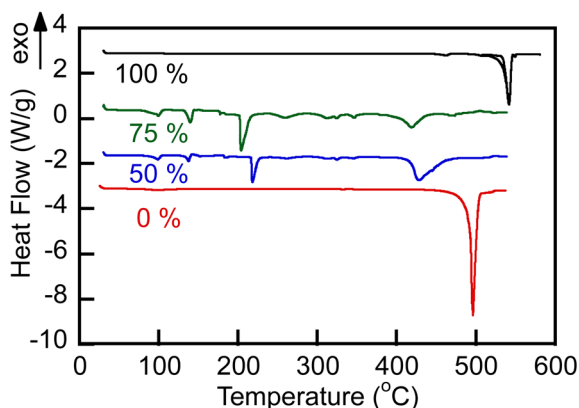


Fig. 3 DSC melting endotherms on 10 °C min⁻¹ heating of the carbonate (Li_{1.24}K_{0.76}CO₃) and borate (Li_{1.5}Na_{1.5}BO₃) and their blends in nitrogen atmosphere. Numbers indicate nominal initial content of borate (mol%) in the blends. Endotherms were shifted along the heat flow axis for the presentation clarity, while preserving the original scale. Solid and dashed lines represent endotherms obtained using a Discovery DSC 250 (sealed pans) and Q600 (open to nitrogen atmosphere), respectively.

stable regenerable molten media for repeated temperature cycling operations.

DSC traces showed (Fig. 3) that all studied salt compositions melted at temperatures below 550 °C, demonstrating sharp melting endotherms. Melting of the eutectic carbonate Li_{1.24}K_{0.76}CO₃ was centered at 496 °C, in excellent agreement with the previously reported data.^{26,27} Borate Na_{1.5}Li_{1.5}BO₃ melting occurred at 539 °C. The borate-carbonate blends (B/C molar ratios 1 : 1 and 3 : 1), as prepared, contained residual hydrate water and melted above 450 °C. The blends recrystallized on cooling at temperatures below 400 °C (cooling exotherms are not shown in Fig. 3). Melting in nitrogen atmosphere enabled removal of crystalline water. Importantly, all materials studied were observed to be consistently liquid at 550 °C under nitrogen atmosphere or in air.

However, due to the reactivity of the borate with CO₂ and its chemical conversion to metaborate while generating alkali metal carbonate, formation of multiple metastable phases upon reaction of the borate component with CO₂ was possible.¹⁷ We thus examined formation of the crystalline phases, if any, in the borate/carbonate blend upon its uptake of and reaction with CO₂ in cooling and subsequent re-melting of the reacted blend (Fig. 4). Reaction was conducted on a platinum pan in 100% CO₂ at 550 °C for 3 h and then the reacted blend sample was cooled at 5 °C min⁻¹ to ambient temperature in a CO₂ atmosphere and the recrystallized material was placed on a zero-background silicon wafer, where XRD was measured at 25 °C (b) and 550 °C, also in a CO₂ atmosphere (c). It was observed that upon reaction of the borate component with CO₂ (eqn (3)), the reacted blend re-melted and demonstrated the absence of any crystalline phases at 550 °C (Fig. 4(c)). This is important for the heating-cooling cycling (temperature swing operation) of the blends in their utilization as regenerable CO₂ sorbents.¹⁷

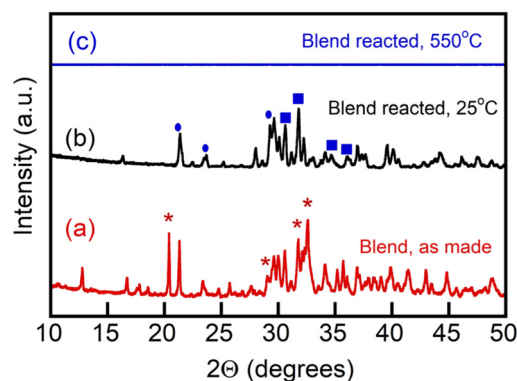


Fig. 4 Diffraction patterns of a blend of Li, Na borate (Li_{1.5}Na_{1.5}BO₃) and Li, K carbonate (Li_{1.24}K_{0.76}CO₃) (1 : 1 mol/mol), as-made (a), the same blend reacted with CO₂ at 550 °C, quenched and measured at 25 °C (b) and the same reacted blend as in (b), but re-melted with XRD measured at 550 °C (c). Asterisks mark peaks matching planes of tetragonal Li and Li, Na tetraborate crystalline phase at 20.4°. Squares designate patterns pertaining to lithium metaborate (LiBO₂). Ovals mark patterns pertaining to lithium carbonate (Li₂CO₃) and Li, NaCO₃ crystal patterns. Crystal pattern references: International Central Securities Depository (ICSD) and JCPDS (Joint Committee on Powder Diffraction Standards) or ICDD (International Centre for Diffraction Data) as follows. ICDD 04-009-3631; ICDD 04-009-6084; ICSD 419673; ICSD 415327; ICSD 65930; ICSD 419673; ICSD 415327; ICSD 16568; ICSD 37060; ICSD 200891.

Viscosity of alkali metal borate/carbonate blends

Alkali (e.g., primarily Li) meta- and tetraborates have been used extensively in a number of applications, primarily as fluxing components for X-ray fluorescence (XRF), atomic emission spectrometry and related analytical techniques.^{34,35} Molten lithium tetraborate generally possesses a high viscosity and tends to solidify as a glass under small temperature gradients.³⁵⁻³⁷ The viscosity of molten lithium borates under temperature gradients is determined by the ratio of optically opaque crystalline matrices and amorphous phases, both with the chemical formula of Li₂B₅O₉.³⁵⁻⁴¹ The amorphous motif can have the structural form of a single tetrahedral boron connected to four oxygen atoms. The oxygen atoms are connected to the trigonal boron species to form a ring with the chemical formula of B₃O₃. In contrast to the alkali metal borates, alkali metal carbonate melts are extremely fluid and the viscosity of the Na₂CO₃, K₂CO₃, and Li₂CO₃ liquids measured by rotational viscometers is on the order of 3–20 mPa s in the 750–1000 °C range and demonstrates Arrhenian behavior.⁴²⁻⁴⁴

In the present work, we were interested in the behavior of blends of the two distinct classes of alkali metal salts, i.e., borates and carbonates, in their molten state under moderate shear stresses and in the lowest temperature range (550–600 °C), wherein both salts are molten. To the best of our knowledge, no reports on the viscosity of blended borate-carbonate melts is available, albeit the viscosities of individual Na_xB_{1-x}O_y (x = 0.75) and (Li_{0.5}Na_{0.5})_xB_{1-x}O_y (x = 0.75) borates in the molten state at 600 °C have been reported by our group.¹²



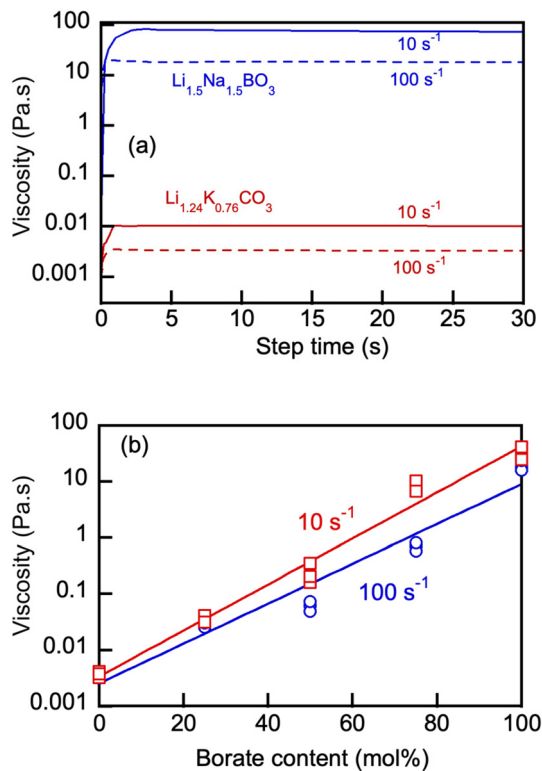


Fig. 5 (a) Rotational viscosity of Li, Na borate ($\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$) and eutectic Li, K carbonate ($\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$) measured at 550 °C and at constant shear rates of 10 and 100 s^{-1} and the effect of borate concentration on viscosity of Li, Na borate ($\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$) and eutectic Li, K carbonate ($\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$) blends at 550 °C and at shear rates of 10 and 100 s^{-1} (b). Numbers denote nominal initial borate concentration (mol%) in the blend. Straight exponent fits ($R^2 > 0.98$) are shown to guide the eye only.

Fig. 5(a) shows representative rotational viscosity measurements of the Li, Na borate ($\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$) and eutectic Li, K carbonate ($\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$) at 550 °C at constant shear rates of 10 and 100 s^{-1} . Pronounced shear-thinning behavior of both molten salts was evident in these measurements, with the borate's viscosity being 3 orders of magnitude larger than that of the carbonate at that temperature. The viscosity of $\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$ measured at constant 100 s^{-1} and 550 and 600 °C was 32 ± 8 ($n = 3$) and 14 ± 5 Pa s ($n = 3$), respectively, which corresponded well with the previously reported data on Li, Na borate at 600 °C.¹²

Variation of the borate content in the blends (Fig. 5(b)) appeared to produce a pronounced effect on the blend viscosity, ranging over 3 orders of magnitude. The results show that eutectic carbonates act as an efficient diluent for the molten alkali metal borates and the blend's viscosity can be adjusted as required for proper handling, pumping, circulation and other operations requiring transport of molten salts at high temperatures, especially in heat transfer and electrolysis applications.

CO₂ uptake by alkali metal borates and their blends with carbonates

The parameters of CO₂ uptake by molten salts were examined with Li, Na borate, $\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$ and its representative blend with the eutectic Li, K carbonate under study, $\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$ (Fig. 6). The uptake of CO₂ (Q , mmol g^{-1}) during temperature was ramped at a very slow rate of 0.33 °C min^{-1} under a flow of 100% CO₂. Prior to the temperature ramp in CO₂, the samples were first purged of water and adsorbed air by exposing them to the N₂ flow and ramping the temperature to 600 °C at 5 °C min^{-1} and then allowing to equilibrate, also under N₂ flow, at 200 °C for 1 h. The slow heating rate enabled precise determination of temperature of the CO₂ uptake onset (T_{on}) and the CO₂ uptake maximum (Q_{max}).

The uptake of CO₂ by Li, Na borate increased dramatically once the temperature was raised to the onset temperature (T_{on}) of 492 °C. After the sharp increase of the CO₂ uptake at T_{on} , the uptake rapidly reached maximum load capacity (Q_{max} , ~ 7.1 mmol g^{-1}) at $T_{\text{max}} = 552$ °C and then after a short plateau started to decrease at higher temperatures starting at 563 °C. Similar behavior was observed with the borate-carbonate blend. However, the presence of $\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$ carbonate in the blend caused a dramatic temperature shift in T_{on} to 395 °C, and the uptake became two-step, increasing first at >395 °C and then more significantly around 460 °C before a final rapid increase, plateau and subsequent decrease. The shift of the T_{on} values in the presence of carbonate in the blend is certainly due the existence of the Li, K carbonate crystals left in the blend after melting and recrystallization that preceded the CO₂ uptake. All crystals are molten above 530 °C (compare with Fig. 4). The Li, K carbonate crystals melt at temperatures much lower than those of the individual borate $\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$ (compare with Fig. 3); the onset of glass transition and melting and the existence of mobile and liquid phases in the salt enables rapid gas-liquid mass exchange and

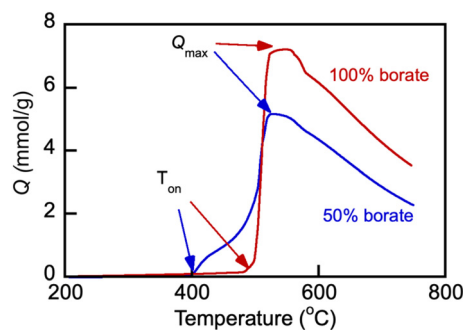


Fig. 6 CO₂ uptake by Li, Na borate ($\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$) and its eutectic Li, K carbonate ($\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$) blend (borate/carbonate ratio, 1 : 1 mol/mol, sample no. 3 in Table 1) under 60 mL min^{-1} flow of 100% CO₂ at a heating rate of 0.33 °C min^{-1} . The CO₂ loading (Q , mmol g^{-1}) was calculated as a sample weight fraction ($10 \times W_f$) gained on the exposure to the CO₂ flow, normalized by the molar mass of CO₂ (44.01 g mol^{-1}). Arrows show the temperature datapoint at which the CO₂ uptake was measured to be at maximum (Q_{max}); T_{on} is the temperature of the CO₂ uptake onset. Numbers indicate nominal initial borate content.



absorption of CO₂ by the melt, which explains the significantly lower T_{on} in the blend vs. that in pure borate.

Fig. 7 shows the effect of varying borate/carbonate blend composition on the CO₂ uptake under a flow of 100% CO₂ at a constant heating rate of 5 °C min⁻¹. The T_{on} scaled with the heating rate (not shown).

As is seen in Fig. 7(b), the addition of eutectic Li_{1.24}K_{0.76}CO₃ carbonate to Li_{1.5}Na_{1.5}BO₃ borate under study lowered the Q_{max} of the blend because the carbonate's ability to physisorb CO₂ in the studied temperature range is low and does not exceed approximately 0.2 mmol g⁻¹. The Q_{max} values increased linearly with the overall borate concentration. However, both T_{on} and T_{max} significantly decreased with the carbonate addition, which indicates that the blends can be operated as reversible absorbents at lower temperatures than pure borates, which is beneficial.

CO₂ absorption in pressure swing cycling operation

Our group discovered that molten alkali metal borates act as reversible liquid absorbents for CO₂ capture in the medium temperature range of 550 to 600 °C, with regenerability over multiple absorption–desorption cycles under both temperature- and pressure-swing operations.^{12,17} Such behavior of the

molten borates in a cyclical absorption–desorption process was ascribed to the “instantaneous” formation of carbonate salts and their subsequent dissociation resulting in carbonate ions being present in the borate without the diffusional transport restrictions imposed by solid product layers characteristic of solid adsorbents.^{11–19}

In the present work, we set out to (i) ascertain whether such cycling would be possible with the borate/carbonate blends, and moreover, (ii) establish whether the carbonate salt added to the borate salt prior to any CO₂ chemisorption, would change the kinetics of the CO₂ upload and desorption.

For the direct comparison, we chose to study a Li, Na borate (Li_{1.5}Na_{1.5}BO₃) and eutectic Li, K carbonate (Li_{1.24}K_{0.76}CO₃) blend (borate/carbonate ratio, 1 : 1 mol mol⁻¹) as representative examples. Both the borate and the blend have been shown to be liquid at 550 °C (Fig. 3 and 4), and hence, the pressure swing cycling was performed at that temperature. The results shown in Fig. 8 demonstrate that both the borate salt alone and its blend with eutectic carbonate exhibited reversible uptake-desorption of CO₂ in the pressure swing operation, within the span of at least 22 cycles. The results were quanti-

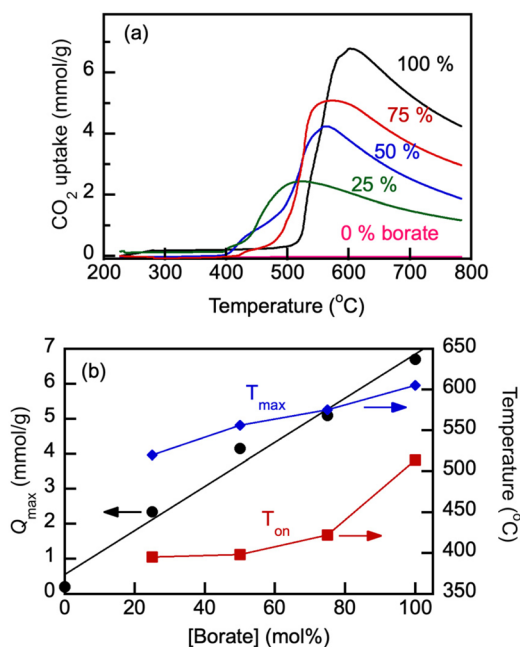


Fig. 7 CO₂ uptake (Q , mmol g⁻¹) by molten borate/carbonate blends under the 60 mL min⁻¹ flow of 100% CO₂ at a heating rate of 5 °C min⁻¹ (a) and dependencies of the maximum CO₂ loading (Q_{max}), temperature of the onset of the loading increase (T_{on}), and the temperature of the maximum CO₂ loading (T_{max}) on nominal content of Li, Na borate, in the borate/carbonate blends (b). In the TGA experiments, the blends were first purged of water and CO₂ by exposing them to N₂ flow and ramping the temperature to 600 °C at 5 °C min⁻¹ and then allowing to equilibrate, also under N₂ flow, at 200 °C for 1 h. The CO₂ loading was calculated as a sample weight fraction gained on the exposure to the CO₂ flow, normalized by the molar mass of CO₂ (44.01 g mol⁻¹). Numbers indicate nominal initial content of borate (mol%) in the blends.

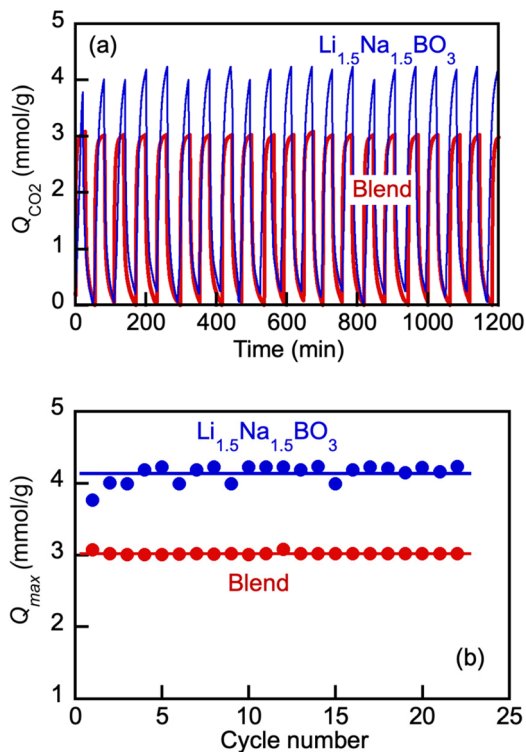


Fig. 8 Effect of cycling on CO₂ uptake by molten Li, Na borate (Li_{1.5}Na_{1.5}BO₃) and eutectic Li, K carbonate (Li_{1.24}K_{0.76}CO₃) blend (borate/carbonate ratio, 1 : 1 mol/mol) (a) and maximum CO₂ loading in each cycle at $t_{\text{cycle}} = 30$ min (Q_{max} , mmol g⁻¹) vs. cycle number (b). Cycling was conducted via pressure swing operation on repeated switching of the gas stream between 100% CO₂ ($p_{\text{CO}_2} = 1$ bar) and 100% N₂ ($p_{\text{CO}_2} = 0$ bar) at 550 °C. Cycle consisted of alternating 30 min of CO₂ flow followed by nitrogen flow (60 mL min⁻¹) for 30 min. The salt samples (6 mg) were evenly spread at the bottom of a platinum pan; temperature 550 °C throughout.



fied with Q_{\max} values defined at the end of each sorption cycle ($t = 30$ min after the instance of the switch to the CO_2 flow) (Fig. 8(b)). As is seen, after the initial 3–4 cycles, the Q_{\max} reached constant values of approximately 4.2 and 3.1 mmol g^{-1} for the borate and the blend, respectively. The lower Q_{\max} values for the blend vs. borate alone are expected (compare with Fig. 7). Importantly, however, the blend did behave as a reversible liquid sorbent. Encouraging by this observation and armed with the knowledge of the dilution effect of the carbonate on the blends' viscosity (Fig. 5), we proceeded to a comparative study of the kinetics of the CO_2 uptake by the borate alone and by the blend in the pressure swing operation.

Detailed comparison of typical CO_2 uptake kinetics in one cycle of the cyclical pressure swing operation shows dramatic differences between the pure borate and the blend kinetics (Fig. 9). Herein, the uptake (Q) is presented *via* the degree of conversion $\alpha = Q/Q_{\max}$; wherein Q_{\max} , mmol g^{-1} , is the maximum CO_2 loading in the cycle at $t_{\text{cycle}} = 30$ min.

Fig. 9(b) shows dramatic differences in the kinetics of the CO_2 uptake between pure borate and its blend with carbonate. The blend absorbed CO_2 very rapidly at the very beginning of the cycle, with high degrees of conversion reached within 1–2 min, whereas with the pure Li, Na borate the initial rate of absorption was low, starting to accelerate at $t > 0.6$ min, which was followed by gradual deceleration of the CO_2 uptake at $t > 15$ min. Analogous results with $\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$ have been previously obtained at 600 °C by our group.¹² The S-shaped uptake kinetics (slow induction rate-acceleration-leveling off period) can be explained by the initial lag time required for dissolution of CO_2 to accumulate carbonate ions (CO_3^{2-}) in the viscous molten borate oxides at sufficient levels to exceed the supersaturation threshold for nucleation and growth of crystal nuclei to form solid Li, Na carbonate particles (LiNaCO_3). In the molten borate-carbonate blend, the carbonate ions are present prior to the onset of the CO_2 uptake and hence, the initial uptake reaches high degrees of conversion.

The overall kinetics of the CO_2 uptake by the molten salts with the nucleation and growth of the carbonate crystalline particles, which can eventually form diffusional barriers for further uptake can be qualitatively described by considering the time intervals over which the uptake rate changes separately.^{12,45,46}

The initial CO_2 uptake can be described by the pseudo first-order reaction kinetics:^{12,45}

$$-\frac{dQ}{dt} = k_1 Q, \quad \text{or after integration,} \quad -\ln(1 - \alpha) = k_1 t \quad (11)$$

where $\alpha = Q/Q_{\max}$.

The kinetics presented in Fig. 9(b) in terms of eqn (11) highlights dramatic differences in the initial uptake rate by the pure borate $\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$ and its blend with carbonate. The blend started absorbing CO_2 instantly and reached high degrees of conversion ($\alpha > 0.7$) at 0.6 min, whereas pure borate showed an induction lag time before starting to uptake CO_2 . The pseudo-first reaction rate constant in the case of the blend

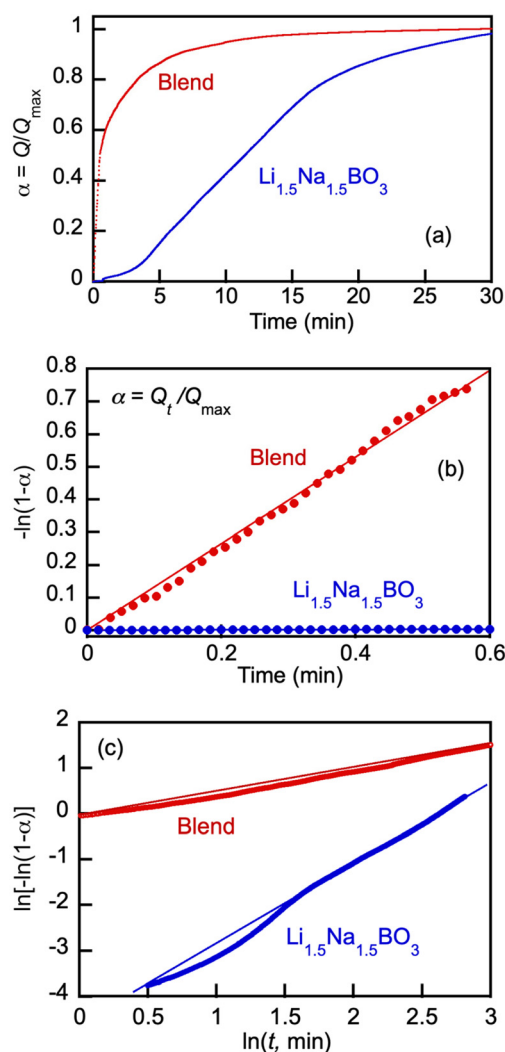


Fig. 9 Typical CO_2 uptake kinetics in one cycle of the cyclical pressure swing operation at 550 °C (a), initial kinetics of CO_2 uptake by Li, Na borate ($\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$) and its blend with eutectic Li, K carbonate ($\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$) (borate/carbonate ratio, 1:1 mol/mol) (blend) presented in terms of eqn (11) (b), and variation of CO_2 conversion degree by Li, Na borate its blend presented in double logarithmic plot of the Avrami-Erofeev equation (eqn (12)) for CO_2 uptake by over the time period of 0.6 min $< t < 15$ min (c). The data is expressed *via* the degree of conversion $\alpha = Q/Q_{\max}$; wherein Q_{\max} , mmol g^{-1} , is the maximum CO_2 loading in the cycle at $t_{\text{cycle}} = 30$ min. Molten salts are Li, Na borate ($\text{Li}_{1.5}\text{Na}_{1.5}\text{BO}_3$) and its blend with eutectic Li, K carbonate ($\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$) (borate/carbonate ratio, 1:1 mol/mol) (blend). Straight lines with $R^2 > 0.98$ goodness-of-fit for the linear regressions (eqn (11)–(13)) are shown.

($k_1 = 1.4 \text{ min}^{-1}$) was 250–300-fold higher than that with pure borate ($k_1 \sim 5 \times 10^{-3} \text{ min}^{-1}$).

The changes in the CO_2 uptake rate after the initial period ($0.6 < t < 15$ min) are described by the well-known Avrami-Erofeev nucleation and nuclei-growth model:^{12,45–48}

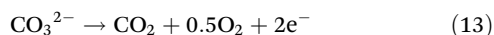
$$-\ln(1 - \alpha) = k_2 \cdot t^n; \quad n = p + m \quad (12)$$





Fig. 11 Cyclic voltammograms (CV) of a galvanized steel cathode in a molten borate and carbonate blend (nominal borate: carbonate mol ratio, 1:1). Borate: $\text{Li}_{1.5}\text{Na}_{1.5}\text{B}_2\text{O}_3$; eutectic Li, K carbonate: $\text{Li}_{1.24}\text{K}_{0.76}\text{CO}_3$. Anode: nickel crucible; temperature: 550 °C. The potential scan started cathodically from 0 V, and the reduction and oxidation sweep directions are shown by arrows (IUPAC convention). Solid blue and dotted red lines show three consecutive scans (scanrate, 10 mV s^{-1}) measured under nitrogen and CO_2 purge, respectively. Designations A and C stand for anodic and cathodic peak potentials, respectively.

temic -0.131 V shift was observed due to the electrochemical cell parameters and conditions relative to the standard potential ($E_{900}^{\circ} = 0$ V) characteristic of the carbonate ion oxidation in molten carbonates:⁵⁷



Reaction (13) is indicated by A1 in Fig. 11. The observed formation of black coating on the anode interior is attributed to the nickel oxidation reaction on the anode-melt interface with the reported standard potential $E_{900}^{\circ} = 0.697$ V:^{58,59}



Reaction (14) is indicated by A2 on the oxidation scan in nitrogen atmosphere in Fig. 15. Lower oxidation currents are observed on the initial scan. Numerous prior studies reported a variety of reduction reactions for nickel compounds (C1) in the presence of neutral gas or carbon dioxide:^{58–62}

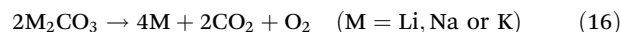


During the cathodic reduction, at potentials in the -1.2 to -0.7 V range nickel oxide dissolves, forming complexes of nickel and carbonate ions. These complexes are reduced to nickel and carbonate ions; the formed nickel is then oxidized in the following anodic scan, at potentials in the 0.7 to 1.2 V range.^{60,62}

The electrochemical processes occurring with nickel and nickel oxide can be considered side reactions, whereas the reactions of electrodeposition of carbon by CO_2 electrolysis are our target product reactions, which will be discussed next. Important deposition potentials of alkali and alkaline earth metals *via* reactions (16) and carbon through reac-

tions (17) in their own molten carbonate salts are well-known.^{23,25}

Electrochemical deposition of metal:

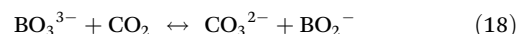


Deposition of carbon *via* carbonate salt decomposition:



In our experiments with borate/carbonate blends in a nitrogen atmosphere, carbon was produced by cathodic reduction of the carbonate anions (reaction eqn (6)) formed by dissociation of the molten alkali metal carbonates (indicated as C2 in the -2.3 V range in Fig. 11). Carbon was deposited on a galvanized steel cathode in significant quantities, along with deposition of alkali metals and boron. The processes of deposition are indicated by C3 in Fig. 11.

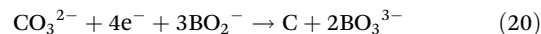
In the presence of the Li, Na borate in the borate/carbonate blend (Fig. 11), borate anions (BO_3^{3-}) formed by dissociation of the borate in the molten salt can mediate the CO_2 capture and subsequently, lead to enhanced chemisorption:



Borate anions also contribute to the metaborate and oxygen anion generation by the molten salt:³¹



Hence, in the presence of the Li, Na borate, the formation of carbonate anions needed for CO_2 electroreduction is augmented, which in turn leads to carbon deposition on the cathode at lower cathodic potentials:



corresponding to the carbonate electroreduction under CO_2 atmosphere in the -1.4 to -1.2 V range and carbon/metal deposition in the -1.8 to -1.5 V range as indicated by C4 and C5, respectively, in Fig. 11. Electroreduction processes in eqn (20) (C4) can be seen as transient, as their peak potentials were lowered with the number of scans, indicating that the majority of the dissolved CO_2 was electroreduced.

The temperature of the electrolysis process with the borate/carbonate blends was fixed at 550 °C, at which the blends exhibited maximum CO_2 uptake at slow rates of heating (Fig. 6). In all experiments, the molten electrolyte was equilibrated with the CO_2 flow prior to the onset of the electrolysis at 550 °C.

The results of the electrolysis conducted at 550 °C in a series of experiments in which the molten salt composition was varied are shown in Fig. 12. The Coulombic efficiency (C_e) results based on the yield of carbon are overlapped with the maximum CO_2 uptake values of the corresponding blend compositions at 550 °C (Q_{max}) measured in TGA experiments. Coulombic efficiency was close to 100% in eutectic Li, K carbonate without the borate added, as expected with galvanized steel cathodes.^{24,25} The yield of carbon in the initially pure Li, K borate at 550 °C was approximately 18% in the borate alone,



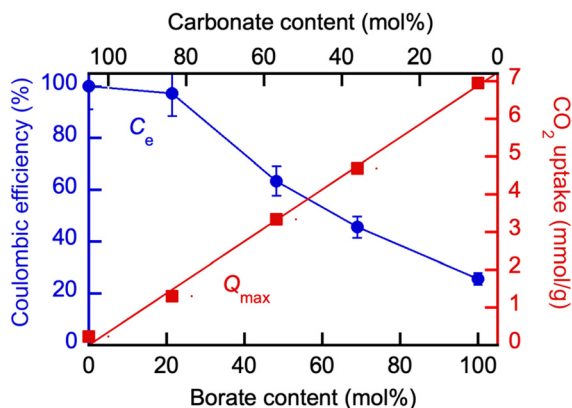


Fig. 12 Effect of the molten borate/carbonate blend composition on the Coulombic efficiency (C_e) of the CO_2 electrolysis and maximum CO_2 uptake (Q_{max}) at 550 °C. Borate: $Li_{1.5}Na_{1.5}B_2O_3$; eutectic Li, K carbonate: $Li_{1.24}K_{0.76}CO_3$. For Q_{max} determination detail, see legend to Fig. 6.

but could be improved by the addition of carbonate $Li_{1.24}K_{0.76}CO_3$ to the blend (Fig. 12). On the other hand, at 20% of the borate added into carbonate, the Coulombic efficiency of the carbon production was close to 100% while the CO_2 uptake was a lot higher than Q_{max} in pure Li, Na carbonate and sufficient for the high yield of the carbon product.

The opposing C_e vs. Q_e trends enable performance optimization *via* the blend composition to trade off the equilibrium CO_2 sorption (capture) uptake with the yield of carbonaceous product during CO_2 electrolysis as measured by Coulombic efficiency.

Structure of the products of CO_2 electrolysis in molten borate/carbonate blends

The products of the CO_2 electrolysis were recovered and purified (see Experimental). Elemental analysis for carbon content in the products varied significantly from approximately 20 to 98 wt% depending on the extent of product purification by washing; concentrations of lithium, zinc and nickel varied in the 0.2 to 3.5 wt%, 0.01–2 wt%, and 0.1–1.5 wt% ranges, respectively.

Fig. 13 shows a general view of the powder XRD pattern of the products of CO_2 electrolysis collected on the galvanized steel cathodes. The broad peaks centered at $2\theta = 26$ – 26.2° observed in the XRD patterns of the electrolysis products obtained with either molten Li, Na borate or Li, K borate or their blends were prominent. The (100) crystal peaks are characteristic of multiwall carbon nanotubes and correspond to a d -spacing between graphene sheets (CNT wall layers) of 3.42–3.46 Å.^{63–65} The XRD patterns of the electrolysis products also featured peaks at $2\theta = 21.3, 30.6,$ and 31.8° , characteristic of the lithium carbonate admixtures that were not removed from the products in the process of purification.⁶⁶ XRD pattern peaks at $2\theta = 34.4$ and 36.2° were due to the presence of ZnO crystals,⁶⁷ formed *via* oxidation of zinc originally present on the galvanized steel cathode surface.⁶⁸ Finally,

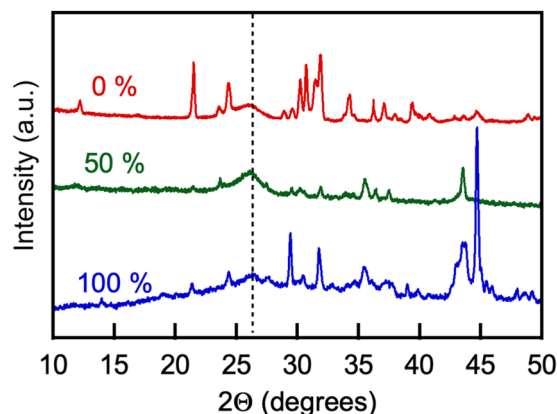


Fig. 13 Representative XRD patterns of the products of CO_2 electrolysis conducted in molten Li, K carbonate ($Li_{1.24}K_{0.76}CO_3$ nominal content of borate, 0 mol%) in borate/carbonate blend (nominal molar carbonate/borate ratio, 1 : 1), and in Li, Na borate ($Li_{1.5}Na_{1.5}B_2O_3$, nominal content of borate, 100 mol%). Borate: $Li_{1.5}Na_{1.5}B_2O_3$; eutectic Li, K carbonate: $Li_{1.24}K_{0.76}CO_3$. Temperature: 550 °C. Cathode: galvanized steel, anode: Ni crucible. Current density on the cathode: 120 mA cm^{-2} . Other conditions are described in Experimental. Numbers stand for nominal molar borate content; dotted vertical line shows graphitic peaks at 26.2° degrees.

peaks that are present in some products at $2\theta = 43.5$ and 44.7° are due to the NiO crystal lattice^{69,70} and Ni electrodeposited onto the product on the cathode from the molten salt solution, respectively. It has been noted previously that zinc and nickel ion admixtures to the molten carbonates mediate the synthesis and contribute to the yield of carbon nanotubes in the process of CO_2 electrolysis.^{7,10}

The products of CO_2 electrolysis were further visualized by means of transmission and scanning electron microscopy (TEM and SEM, Fig. 14). Images demonstrated multiwalled CNT (MWCNT) obtained in all borate/carbonate compositions at 550 °C. The MWCNT possessed 10–16 graphene layers, with walls approximately 4.5–5 nm thick, and diameters of ~15.5 nm. Similar MWCNT have been observed previously in the products of CO_2 electrolysis conducted in alkali metal carbonates only, without borates.^{7,10}

Raman spectra of our electroreduction products (Fig. 15) showed a strong peak at around 1580 cm^{-1} (G-band, arising from the sp^2 carbon stretching of the C–C bond) and an additional band at 1350 cm^{-1} (D-band caused by the disordered structure of graphene). The presence of the G-band Raman feature is typical of all graphite-like materials, including multiwall CNT.^{71,72} The presence of the peak at around 2690 cm^{-1} , corresponding to the G' band, is more specific to small crystallites in CNT. The G-peak of the products prepared in 75 mol% initial borate composition was somewhat broader than the one observed in the spectra of the product obtained in the 1 : 1 borate/carbonate blend (borate content, 50 mol%), and some splitting of the G-peak into two peaks, centered at 1585 cm^{-1} and 1610 cm^{-1} (D'-peak) was apparent. This can be explained by the presence of the amorphous carbon impurities





Fig. 14 TEM (a) and SEM (b) microphotographs of MWCNT found in the products of CO₂ electrolysis conducted in borate (Li_{1.5}Na_{1.5}BO₃) and eutectic carbonate (Li_{1.24}K_{0.76}CO₃) blend (1 : 1 mol/mol) at 550 °C.

on the graphitic layers of the CNT, which were observed by SEM. Overall, Raman spectra (Fig. 15), together with the XRD (Fig. 13) and electron microscopy (Fig. 14), provide unequivocal evidence of the presence of carbon nanotubes in the products of our CO₂ electroreduction process.

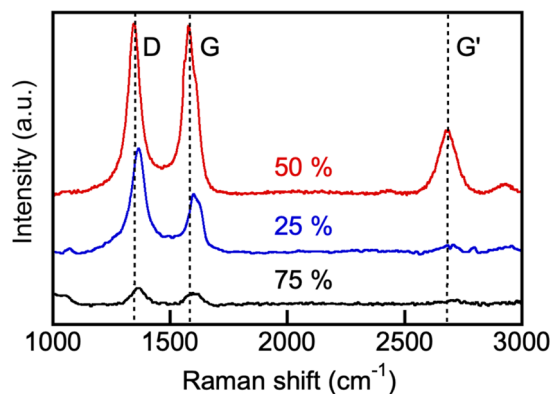


Fig. 15 Raman spectra of the products of CO₂ electrolysis conducted in borate (Li_{1.5}Na_{1.5}BO₃) and eutectic carbonate (Li_{1.24}K_{0.76}CO₃) blends at 550 °C. Numbers indicate the initial borate concentration in the blend (mol%). For other detail, see Experimental.

Conclusions

A family of blended compositions of molten alkali metal borates and carbonates has been examined as reversible CO₂ absorbents as well as media for the CO₂ electrolysis for carbon conversion. Salt structure, reactions with CO₂ and viscosity were studied. Blended borate (Li_{1.5}Na_{1.5}BO₃) and eutectic Li, K carbonate (Li_{1.24}K_{0.76}CO₃) compositions are molten in the 550–600 °C (medium) temperature range. These compositions can be applied as reversible molten absorbents of CO₂, without a significant deterioration of the capture capacity over many cycles of the pressure swing operation. Addition of carbonates to the molten borate lowers overall CO₂ uptake due to the lower sorption capacity of carbonate. However, the addition of eutectic carbonates to the molten Li, Na borate (i) lowers the melt viscosity and enables lowering of the temperature of the pressure swing operation as well as (ii) dramatically accelerates the CO₂ uptake at the initial stage of the cycle, potentially enabling a faster cycling. Blended borate/carbonate compositions were found that possess simultaneous maximum loading capacity for CO₂ and enable maximum product (multiwall carbon nanotube) yield at medium temperatures (550°).

The blended borate/carbonate compositions described herein can find utility in processes involving both carbon capture and CO₂ capture/utilization applications. For the reversible capture plant design, the most influential parameters are the cost of CO₂ handling (transport and storage), the cost of electricity, and the energy required for the separation.¹⁹ For the CCUS processes involving both capture and conversion designs, the cost of electricity is the most important factor. Given that a very large amount of electrical energy is required for this design, it must be supplied by renewable energy.^{5,7,3} The high coulombic efficiency (over 90%, Fig. 12) achieved with some of the borate/carbonate blends is also a very influential factor. Our future efforts will focus on the search for the cost-optimum molten salt materials for CCUS in the medium to low temperature ranges.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

- W. Weng, B. Jiang, Z. Wang and W. Xiao, *Sci. Adv.*, 2020, 6(9), eaay9278, DOI: [10.1126/sciadv.aay9278](https://doi.org/10.1126/sciadv.aay9278).



- 2 S. Jing, M. Wang and W. Xiao, *J. Energy Chem.*, 2022, **64**, 404, DOI: [10.1016/j.jechem.2021.05.012](https://doi.org/10.1016/j.jechem.2021.05.012).
- 3 W. Weng, L. Tang and W. Xiao, *J. Energy Chem.*, 2019, **28**, 128, DOI: [10.1016/j.jechem.2018.06.012](https://doi.org/10.1016/j.jechem.2018.06.012).
- 4 S. Licht, X. Liu, G. Licht, X. Wang, A. Swesi and Y. Chan, *Mater. Today Sustainability*, 2019, **6**, 100023.
- 5 J. Ren, A. Yu, P. Peng, M. Lefler, F.-F. Li and S. Licht, *Acc. Chem. Res.*, 2019, **52**(11), 3177, DOI: [10.1021/acs.accounts.9b00405](https://doi.org/10.1021/acs.accounts.9b00405).
- 6 S. Licht, Carbon dioxide to carbon nanotube scale-up, arXiv, 2017, preprint, arXiv:1710.07246.
- 7 J. Ren and S. Licht, *Sci. Rep.*, 2016, **6**, 27760.
- 8 X. Chen, Z. Zhao, J. Qu, B. Zhang, X. Ding, Y. Geng, H. Xie, D. Wang and H. Yin, *ACS Sustainable Chem. Eng.*, 2021, **9**, 4167, DOI: [10.1021/acssuschemeng.1c00028](https://doi.org/10.1021/acssuschemeng.1c00028).
- 9 X. Wang, X. Liu, G. Licht, B. Wang and S. Licht, *J. CO2 Util.*, 2019, **34**, 303, DOI: [10.1016/j.jcou.2019.07.007](https://doi.org/10.1016/j.jcou.2019.07.007).
- 10 J. Johnson, M. Ren, G. Lefler, G. Licht, J. Vicini, X. Liu and S. Licht, *Mater. Today Energy*, 2017, **5**, 230, DOI: [10.1016/j.mtener.2017.07.003](https://doi.org/10.1016/j.mtener.2017.07.003).
- 11 T. Harada and T. A. Hatton, Carbon dioxide removal using lithium borate, *US Patent*, 10913658, 2021.
- 12 T. Harada, C. Halliday, A. Jamal and T. A. Hatton, *J. Mater. Chem. A*, 2019, **7**, 21827, DOI: [10.1039/C9TA09122J](https://doi.org/10.1039/C9TA09122J).
- 13 T. Harada and T. A. Hatton, *J. Mater. Chem. A*, 2017, **5**, 22224, DOI: [10.1039/C7TA06167F](https://doi.org/10.1039/C7TA06167F).
- 14 C. Halliday, N. Ozbek and T. A. Hatton, *ACS Appl. Mater. Interfaces*, 2020, **12**, 51468, DOI: [10.1021/acsami.0c14633](https://doi.org/10.1021/acsami.0c14633).
- 15 C. Halliday, T. Harada and T. A. Hatton, *Ind. Eng. Chem. Res.*, 2020, **59**, 8937, DOI: [10.1021/acs.iecr.0c01140](https://doi.org/10.1021/acs.iecr.0c01140).
- 16 C. Halliday, T. Harada and T. A. Hatton, *Environ. Sci. Technol.*, 2020, **54**, 6319, DOI: [10.1021/acs.est.0c01671](https://doi.org/10.1021/acs.est.0c01671).
- 17 C. Halliday, T. Harada and T. A. Hatton, *Chem. Mater.*, 2019, **32**, 348, DOI: [10.1021/acs.chemmater.9b03876](https://doi.org/10.1021/acs.chemmater.9b03876).
- 18 C. Halliday and T. A. Hatton, *Ind. Eng. Chem. Res.*, 2021, **60**(26), 9313, DOI: [10.1021/acs.iecr.1c00597](https://doi.org/10.1021/acs.iecr.1c00597).
- 19 C. Halliday and T. A. Hatton, *Appl. Energy*, 2020, **280**, 116016, DOI: [10.1016/j.apenergy.2020.116016](https://doi.org/10.1016/j.apenergy.2020.116016).
- 20 S. W. Martin, E. I. Cooper and C. A. Angell, *J. Am. Ceram. Soc.*, 1983, **66**, c153, DOI: [10.1111/j.1151-2916.1983.tb10622.x](https://doi.org/10.1111/j.1151-2916.1983.tb10622.x).
- 21 M. P. Nitzsche, L. Bromberg and T. A. Hatton, Capture and electrochemical conversion of CO₂ into carbon nanotubes using molten alkali metal borates, *Amer. Chem. Soc. Fall Meeting*, Chicago, IL, 08.21.2022.
- 22 J. Ren, J. Lau, M. Lefler and S. Licht, *J. Phys. Chem. C*, 2015, **119**, 23342, DOI: [10.1021/acs.jpcc.5b07026](https://doi.org/10.1021/acs.jpcc.5b07026).
- 23 H. Yin, X. Mao, D. Tang, W. Xiao, L. Xing, H. Zhu, D. Wang and D. R. Sadoway, *Energy Environ. Sci.*, 2013, **6**, 1538–1545, DOI: [10.1039/C3EE24132G](https://doi.org/10.1039/C3EE24132G).
- 24 X. Liu, G. Licht, X. Wang and S. Licht, *Catalysts*, 2022, **12**, 137, DOI: [10.3390/catal12020137](https://doi.org/10.3390/catal12020137).
- 25 H. V. Ijije, R. C. Lawrence and G. Z. Chen, *RSC Adv.*, 2014, **4**, 35808, DOI: [10.1039/C4RA04629C](https://doi.org/10.1039/C4RA04629C).
- 26 C. Chen, T. Tran, R. Olivares, S. Wright and S. Sun, *J. Sol. Energy Eng.*, 2014, **136**(3), 031017, DOI: [10.1115/1.4027264](https://doi.org/10.1115/1.4027264), (7 pages).
- 27 G. J. Janz and M. R. Lorenz, *J. Chem. Eng. Data*, 1961, **6**(3), 321, DOI: [10.1021/je00103a001](https://doi.org/10.1021/je00103a001).
- 28 G. Argandoña, M. Aresti, J. M. Blanco, E. Muel and J. Esarte, *Appl. Sci.*, 2021, **11**, 7597, DOI: [10.3390/app11167597](https://doi.org/10.3390/app11167597).
- 29 M. Loubser, C. Strydom and H. A. Potgieter, *X-Ray Spectrom.*, 2004, **33**, 212, DOI: [10.1002/xrs.700](https://doi.org/10.1002/xrs.700).
- 30 X. Wang, X. Liu, G. Licht and S. Licht, *Sci. Rep.*, 2020, **10**, 15146, DOI: [10.1038/s41598-020-71644-0](https://doi.org/10.1038/s41598-020-71644-0).
- 31 L. Hu, B. Deng, K. Du, R. Jiang, Y. Dou and D. Wang, *iScience*, 2020, **23**, 101607, DOI: [10.1016/j.isci.2020.101607](https://doi.org/10.1016/j.isci.2020.101607).
- 32 L. Hu, B. Deng, Z. Yang and D. Wang, *Electrochem. Commun.*, 2020, **121**, 106864, DOI: [10.1016/j.elecom.2020.106864](https://doi.org/10.1016/j.elecom.2020.106864).
- 33 N. Khalizadeh, E. B. Saion, H. Mirabolghasemi, A. H. B. Shaari, M. B. Hashim, M. B. H. Ahmad, N. M. Ali and A. Dehzangi, *J. Mater. Res. Technol.*, 2016, **5**, 37, DOI: [10.1016/j.jmrt.2015.05.005](https://doi.org/10.1016/j.jmrt.2015.05.005).
- 34 F. Claisse, *Powder Diffr.*, 2006, **21**(2), 181, DOI: [10.1154/1.2219872](https://doi.org/10.1154/1.2219872).
- 35 E. Braysher, B. Russell, S. Woods, M. García-Miranda, P. Ivanov and D. Read, *J. Radioanal. Nucl. Chem.*, 2019, **321**, 183, DOI: [10.1007/s10967-019-06572-z](https://doi.org/10.1007/s10967-019-06572-z).
- 36 Y. Anzai, K. Terashima and S. Kimura, *J. Cryst. Growth*, 1993, **134**, 235, DOI: [10.1016/0022-0248\(93\)90131-F](https://doi.org/10.1016/0022-0248(93)90131-F).
- 37 J. Filipiak, A. Majchrowski and T. Łukasiewicz, *Arch. Acoust.*, 1994, **19**, 131 <https://acoustics.ippt.pan.pl/index.php/aa/article/view/1067/904>.
- 38 K. Byrappa and K. V. K. Shekar, Phases and crystallization in the system Li₂O-B₂O₃-H₂O under hydrothermal conditions, *J. Mater. Res.*, 1993, **8**, 864–870, DOI: [10.1557/JMR.1993.0864](https://doi.org/10.1557/JMR.1993.0864).
- 39 P. J. Bray, S. A. Feller, G. E. Jellison and Y. H. Yun, *J. Non-Cryst. Solids*, 1980, **39**, 93, DOI: [10.1016/0022-3093\(80\)90400-7](https://doi.org/10.1016/0022-3093(80)90400-7).
- 40 A. Senyshyn, B. Schwarz, T. Lorenz, V. T. Adamiv, Y. V. Burak, J. Banyś, R. Grigalaitis, L. Vasylechko, H. Ehrenberg and H. Fuess, *J. Appl. Phys.*, 2010, **108**, 093524, DOI: [10.1063/1.3504244](https://doi.org/10.1063/1.3504244).
- 41 B. Chen, U. Werner-Zwanziger, M. L. F. Nascimento, L. Ghussn, E. D. Zanotto and J. W. Zwanziger, *J. Phys. Chem. C*, 2009, **113**, 20725, DOI: [10.1021/jp907259e](https://doi.org/10.1021/jp907259e).
- 42 D. Di Genova, C. Cimarelli, K.-U. Hess and D. B. Dingwell, *Am. Mineral.*, 2016, **101**, 953, DOI: [10.2138/am-2016-5537CCBYNCND](https://doi.org/10.2138/am-2016-5537CCBYNCND).
- 43 S. W. Kim, K. Uematsu, K. Toda and M. Sato, *J. Ceram. Soc. Jpn*, 2015, **143**, 355, DOI: [10.2109/jcersj2.123.355](https://doi.org/10.2109/jcersj2.123.355).
- 44 G. J. Janz and J. Saegusa, *J. Electrochem. Soc.*, 1963, **110**, 452, DOI: [10.1149/1.2425785](https://doi.org/10.1149/1.2425785).
- 45 T. Harada, F. Simeon, E. Z. Hamad and T. A. Hatton, *Chem. Mater.*, 2015, **27**(6), 1943, DOI: [10.1021/cm503295g](https://doi.org/10.1021/cm503295g).
- 46 W. Gao, M. A. Vasiliades, C. M. Damaskinos, M. Zhao, W. Fan, Q. Wang, T. R. Reina and A. M. Efstathiou, *Environ. Sci. Technol.*, 2021, **55**(8), 4513, DOI: [10.1021/acs.est.0c08731](https://doi.org/10.1021/acs.est.0c08731).
- 47 T. J. W. D. Bruijn, W. A. D. Jong and P. J. V. D. Berg, *Thermochim. Acta*, 1981, **45**, 315–325, DOI: [10.1016/0040-6031\(81\)85091-5](https://doi.org/10.1016/0040-6031(81)85091-5).



- 48 A. Khawam and D. R. Flanagan, *J. Phys. Chem. B*, 2006, **110**, 17315, DOI: [10.1021/jp062746a](https://doi.org/10.1021/jp062746a).
- 49 M. Lefler and C. L. Pint, *ACS Cent. Sci.*, 2016, **2**, 162, DOI: [10.1021/acscentsci.5b00400](https://doi.org/10.1021/acscentsci.5b00400).
- 50 J. Ren, F.-F. Li, J. Lau, L. González-Urbina and S. Licht, *Nano Lett.*, 2015, **15**, 6142, DOI: [10.1021/acs.nanolett.5b02427](https://doi.org/10.1021/acs.nanolett.5b02427).
- 51 S. Licht, B. Wang, S. Ghosh, H. Ayub, D. Jiang and J. Ganley, *J. Phys. Chem. Lett.*, 2010, **1**, 2363, DOI: [10.1021/jz100829s](https://doi.org/10.1021/jz100829s).
- 52 Z. Li, D. Yuan, H. Wu, W. Li and D. Gu, *Inorg. Chem. Front.*, 2018, **5**, 208, DOI: [10.1039/C7QI00479F](https://doi.org/10.1039/C7QI00479F).
- 53 V. N. Tare and J. B. Wagner, *J. Appl. Phys.*, 1983, **54**, 6459, DOI: [10.1063/1.331927](https://doi.org/10.1063/1.331927).
- 54 S. M. A. Shibli, B. N. Meena and R. Remya, *Surf. Coat. Technol.*, 2015, **262**, 210, DOI: [10.1016/j.surfcoat.2014.12.054](https://doi.org/10.1016/j.surfcoat.2014.12.054).
- 55 P. Wang, Y. Liu, Z. Li, D. Ji, Z. Qiao, J. Zhang, Q. Jia and H. Wu, *J. Electrochem. Soc.*, 2021, **168**, 083501, DOI: [10.1149/2.0861910jes](https://doi.org/10.1149/2.0861910jes).
- 56 F. M. Chang, S. Brahma, J. H. Huang, Z. Z. Wu and K.-Y. Lo, *Sci. Rep.*, 2019, **9**, 905, DOI: [10.1038/s41598-018-37601-8](https://doi.org/10.1038/s41598-018-37601-8).
- 57 R. Wartena, J. Winnick and P. H. Pfromm, *J. Appl. Electrochem.*, 2002, **32**, 415, DOI: [10.1023/A:1016334307899](https://doi.org/10.1023/A:1016334307899).
- 58 Y. Izaki, Y. Mugikura, T. Watanabe, M. Kawase and J. R. Selman, *J. Power Sources*, 1998, **75**, 236, DOI: [10.1016/S0378-7753\(98\)00117-7](https://doi.org/10.1016/S0378-7753(98)00117-7).
- 59 M. D. Ingram and G. I. Janz, *Electrochim. Acta*, 1965, **10**, 783, DOI: [10.1016/0013-4686\(65\)80043-3](https://doi.org/10.1016/0013-4686(65)80043-3).
- 60 M. S. Yazici and J. R. Selman, *J. Electroanal. Chem.*, 1998, **457**, 89, DOI: [10.1016/S0022-0728\(98\)00126-0](https://doi.org/10.1016/S0022-0728(98)00126-0).
- 61 J. P. T. Vossen, L. Plompond and J. H. W. de Wit, *J. Electrochem. Soc.*, 1994, **141**, 3040, DOI: [10.1149/1.2059276](https://doi.org/10.1149/1.2059276).
- 62 Q. Li, F. Borup, I. Petrushina and N. Bjerrum, *J. Electrochem. Soc.*, 1999, **146**, 2449, DOI: [10.1149/1.1391954](https://doi.org/10.1149/1.1391954).
- 63 B. D. Che, B. Q. Nguyen, B. Q. Nguyen, L. T. Nguyễn, L. T. Nguyễn and N. H. Nguyen, *Chem. Cent. J.*, 2015, **9**, 10, DOI: [10.1186/s13065-015-0087-2](https://doi.org/10.1186/s13065-015-0087-2).
- 64 G. Xu, Z.-C. Feng, Z. Popovic, J.-Y. Lin and J. J. Vittal, *Adv. Mater.*, 2001, **13**, 264, DOI: [10.1002/1521-4095\(200102\)13:4<264](https://doi.org/10.1002/1521-4095(200102)13:4<264).
- 65 D. N. Futaba, T. Yamada, K. Kobashi, M. Yumura and K. Hata, *J. Am. Chem. Soc.*, 2011, **133**, 5716, DOI: [10.1021/ja2005994](https://doi.org/10.1021/ja2005994).
- 66 W. Cai, R. Chen, Y. Yang, M. Yi and L. Xiang, *Crystals*, 2018, **8**, 19, DOI: [10.3390/cryst8010019](https://doi.org/10.3390/cryst8010019).
- 67 JCPDS #79-0206, #36-1451.
- 68 P. Rajasekaran, H. Kannan, S. Das, M. Young and S. Santra, *AIMS Environ. Sci.*, 2016, **3**, 439, DOI: [10.3934/environsci.2016.3.439](https://doi.org/10.3934/environsci.2016.3.439).
- 69 S. Rakshit, S. Ghosh, S. Chall, S. S. Mati, S. P. Moulik and S. C. Bhattacharya, *RSC Adv.*, 2013, **3**, 19348, DOI: [10.1039/C3RA42628A](https://doi.org/10.1039/C3RA42628A).
- 70 V. D. Jović, V. Maksimović, M. G. Pavlović and K. I. Popov, *J. Solid State Electrochem.*, 2006, **10**, 373, DOI: [10.1007/s10008-005-0687-1](https://doi.org/10.1007/s10008-005-0687-1).
- 71 E. F. Antunes, A. O. Lobo, E. J. Corat, V. J. Trava-Airoldi, A. A. Martin and C. Verissimo, *Carbon*, 2006, **44**, 2202, DOI: [10.1016/j.carbon.2006.03.003](https://doi.org/10.1016/j.carbon.2006.03.003).
- 72 M. S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus and R. Saito, *Nano Lett.*, 2010, **10**, 751, DOI: [10.1021/nl904286r](https://doi.org/10.1021/nl904286r).
- 73 S. Licht, arXiv, 2019, preprint, arXiv:1901.07134.

