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Paired production of formic acid/formate by cathodic reduction of CO_2 at Sn and anodic oxidation of methanol at BDD

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ABSTRACT

The paired synthesis of formic acid/formate (FA) via CO_2 cathodic reduction and methanol anodic oxidation was investigated using a tin cathode and, for the first time, a boron doped diamond (BDD) anode. To select the most suitable operative conditions for the paired process, the influence of several parameters, such as the nature of the supporting electrolyte (SE), the concentration of both SE and CH_3OH, and the temperature, was studied in detail for both cathodic and anodic processes. In particular, the effect of SE nature was thoroughly evaluated by testing SEs containing different cations (K^+, Na^+ and Cs^+) and anions (SO_4^{2-}, OH^-, and HCO_3^-). The results show that the use of a BDD anode and of a tin cathode allows to obtain very high faradic efficiencies for both cathodic and anodic processes under optimized operating conditions, especially when operating with 0.1 M Na_2SO_4 as SE in the catholyte and 0.5 M NaOH + 0.5 M CH_3OH in the anolyte.

1. Introduction

Numerous research efforts worldwide are focused on defining effective routes to convert CO_2 into valuable chemicals [1–4]. Electrochemical paths, where both anodic and cathodic processes are simultaneously exploited to produce high value products (named paired electrochemical processes, PEP), are particularly promising to improve the economic perspectives of the electrochemical conversion of CO_2 [5–14]. However, relevant improvements of existing processes are necessary to achieve high selectivity and faradic efficiencies (FE) for both anodic and cathodic processes as well as high productivity and stability.

Recently, some interesting publications were focused on the production of formic acid or formate (FA) by cathodic reduction of CO_2 (eq. (1)) ($ERCO_2$) and anodic oxidation of methanol (MeOH) (eqs. (2) and (3) in basic and acidic conditions, respectively) (MOR) [15–18].

$$CO_2 + 2H^+ + 2e^- = HCOOH \text{ or } HCOO^- + H^+ \ (K_a = 1.8 \times 10^{-4}) \quad (1)$$

$$CH_3OH + 5OH^- = HCOO^- + 4H_2O + 4e^- \quad (2)$$

$$CH_3OH + H_2O = HCOOH + 4H^+ + 4e^- \quad (3)$$

Formic acid and formate salts are widely used in many sectors, such as agriculture, textile, and plastics and pharmaceutical industries [19]. They command a markedly higher market price than both CO_2 and MeOH [20,21]. When integrated into paired electrochemical processes (PEP), this approach enhances overall energy efficiency and product selectivity. Moreover, MOR proceeds at much lower anodic potentials ($E^\circ = +0.016$ V vs SHE) than the oxygen evolution reaction (OER), which is limited by sluggish kinetics and requires substantial overpotentials [18]. This imbalance results in the OER consuming up to over 90% of the total electrical input, with CO_2 conversion utilizing only the residual share [10]. Various cathodes were tested up to now for the production of FA by PEP. For example, a Bi nanoparticles (Bi NPs) cathode and a $Ni(OH)_2$ anode were used to simultaneously produce FA in the anodic and cathodic compartments of a divided cell [15]. Wei and coauthors investigated this process using copper oxide nanosheets grown on copper foam (CuONS/CF) as anode and mesoporous tin dioxide grown on carbon cloth ($mSnO_2$/CC) as cathode [16], while CuO/copper foam and Bi metal–organic frameworks were used as an anode and cathode, respectively, by Cao et al. [17]. In this work, we investigated the paired synthesis of FA via CO_2 reduction at a tin cathode and, for the first time, to the best of our knowledge, methanol anodic oxidation at a boron doped diamond (BDD) anode.

Compared with more conventional electrodes, BDD electrodes

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present some advantages including a large potential window, high current efficiency, a very good stability in aggressive media and the ability to produce different reactive species, which makes them a remarkably versatile platform for anodic electrochemical processes [22,23]. BDD anodes were previously widely investigated for various purposes including:

- the treatment of numerous kinds of wastewater by mineralization of organics contained in these matrices [22,24];
- disinfection of water solutions [24];
- the synthesis of various compounds by both anodic oxidation and cathodic reduction [25–27].

It was shown that the oxidation of various organics, including phenolic compounds, in aqueous solutions at BDD anodes results in the production of carboxylic acids [19] that are more resistant to oxidation than the starting compounds [28,29], thus giving rise to their accumulation. The oxidation of MeOH at BDD was rarely reported. Kapalka et al. have studied MeOH oxidation at BDD anodes in 1 M $HClO_4$ [30,31]. They have shown that oxidation of the alcohol at BDD occurs mainly at the potentials of OER (eqs. (4) and (5)), where a significant production of hydroxyl radicals takes place at the electrode (eq. (4)), thus favouring the oxidation of MeOH (eq. (6)), which is converted into methyl formate and CO_2 [30].

$$BDD + H_2O \rightarrow BDD(HO^*) + H^+ + e^- \quad (4)$$

$$BDD(HO^*) \rightarrow BDD + ½\ O_2 + H^+ + e^- \quad (5)$$

$$BDD(HO^*) + R \rightarrow BDD + RO + H^+ + e^- \quad (6)$$

Anodic oxidation of small organic molecules, such as MeOH, at BDD is often investigated in the framework of wastewater treatment with the aim to favour their mineralization. In this study, we demonstrate that BDD anodes can also be used to produce selectively FA with good faradic efficiencies. In particular, we aim to provide a detailed investigation of the PEP, focusing on the production of FA via both MOR at BDD anodes and $ERCO_2$ at Sn cathodes. We evaluated the influence of several operating parameters on the anodic and cathodic formation of FA. In particular, a systematic assessment of the role of the SE was carried out by analysing the effects of the cationic and anionic species on both the cathodic and the anodic processes. In addition, the impacts of SE concentration, CH_3OH concentration, and temperature were examined.

2. Experimental section

2.1. Reagents, experimental apparatus and electrolysis

Potassium sulfate (K_2SO_4, ≥99.9; CAS No. 7778-80-5), sodium sulfate (Na_2SO_4, >99%; CAS No. 7757-82-6), potassium bicarbonate ($KHCO_3$, ≥99.7%; CAS No. 298-14-6), and methanol (CH_3OH, HPLC-grade; CAS No. 67-56-1) were supplied by Carlo Erba. Cesium sulfate (Cs_2SO_4, ≥99.7%; CAS No. 10294-54-9) was purchased from Thermo Scientific. Potassium hydroxide (KOH, 85%; CAS No. 1310-58-3) and sodium hydroxide (NaOH, ≥97%; CAS No. 1310-73-2) were obtained from J.T. Baker and Sigma-Aldrich, respectively. All electrodes were cleaned prior to use by immersion in HPLC-grade water and brief ultrasonic treatment (5 min). For tin cathodes, a mechanical polishing step preceded the sonication to ensure reproducible surface conditions.

Electrochemical experiments were carried out in a two-chamber glass reactor as reported in [18], in which the anodic and cathodic compartments were separated by a Nafion® 324 cation-exchange membrane. A boron-doped diamond (BDD, Condias, Itzehoe, Germany) plate was employed as the anode, whereas the cathode was a tin sheet (Carlo Erba). Both electrodes had a geometric surface area of 2.4 cm^2. Each half-cell contained 75 mL of electrolyte solution and a headspace volume of 37 mL. The catholyte was continuously saturated with high-purity CO_2 (Rivoira, 99.999%), while the anolyte consisted of aqueous CH_3OH solutions prepared at different concentrations. All electrolyses were carried out under quiescent conditions without mechanical stirring. Galvanostatic tests were performed for 2 h at a fixed current density of 11 mA cm^{-2}, using an Amel potentiostat/galvanostat (model 2549). Potentiostatic tests were performed for 2 h at BDD anode by applying a fixed potential of 1.25 V or 1.8 V vs SCE in KOH, or 2.0 V vs SCE in Na_2SO_4, using the same experimental setup used for the galvanostatic tests. Cyclic voltammetry (CV) measurements were carried out using an Autolab PGSTAT12 potentiostat/galvanostat equipped with NOVA software (Metrohm AG, The Netherlands). CVs were carried out in an undivided 50 mL glass cell equipped with a platinum counter electrode and a saturated calomel electrode (SCE) as the reference electrode. A BDD plate with a geometric surface area of 0.1 cm^2 was employed as the working electrode. The electrolytes investigated were 0.1 M KOH and Na_2SO_4. Methanol was subsequently added to reach concentrations of 5, 50, and 500 mM. CVs were recorded over a potential range of 0–2.0 V vs SCE, performing 10 consecutive scans at a scan rate of 0.1 V s^{-1}.

All experiments were performed at room temperature (24°C). Temperature effects were explored by operating the system at 2, 6, 13, 24 and 35°C. Low temperature was maintained using an ice-bath setup, whereas experiments at 35°C were performed using a thermostated heating plate (VELP Scientifica).

To ensure data reliability, each electrolysis condition was replicated at least twice and the average results were reported.

2.2. Analyses methods and performances

The concentration of FA in the liquid phase was quantified by High-Performance Liquid Chromatography (HPLC), using an Agilent 1260 instrument equipped with a Rezex ROA–Organic Acid H^+ (8%) column. Chromatographic analyses were carried out at 20°C, employing a UV detector set at 210 nm. A 0.005 N aqueous H_2SO_4 (Carlo Erba, 98%, CAS No. 7664-93-9) solution (pH 2.5) was used as the mobile phase at a flow rate of 0.5 mL min^{-1}. Under these conditions, FA exhibited a retention time of approximately 18.5 min.

The CO and CO_2 produced were quantified by gas chromatography (GC). Gas-phase analyses were performed every 30 min, including a sample at $t = 0$. Gas samples were withdrawn through a pierceable septum fitted to the electrochemical cell, from the headspace of the anodic compartment. Analyses were carried out using a Supelco Carboxen® 60/80 packed column. The oven was operated under a three-stage program: 35°C for 5 minutes, followed by a ramp to 225°C at 20°C min^{-1}, and a final hold at 225°C for 8 minutes. The TCD was operated at 230°C, with helium (99.999%) as the carrier gas at 1 bar. Gas samples were injected with a 50 µL Hamilton GasTight syringe.

Solution pH was monitored using a Checker® pH Tester (model HI98103, HANNA®).

Process performance was assessed through the Faradic Efficiency (FE) of FA and CO formation, calculated as [18,32]:

$$FE_{FA} = n * F * V * [FA]/(I * t) * 100 \quad (7)$$

$$FE_{CO} = n * F * V * [CO]/(I * t) * 100 \quad (8)$$

where n is the number of electrons involved (2 for FA produced via CO_2 reduction; 4 for FA and CO generated from methanol oxidation), F is Faraday's constant (96485 C mol^{-1}), V refers to the volume of the liquid solution (75 mL) for FA analysis or volume of the headspace (37 mL) for analysis of gas phase components, [FA] and [CO] are the concentrations (mol L^{-1}), I is the applied current (A), and t is the electrolysis time (s).

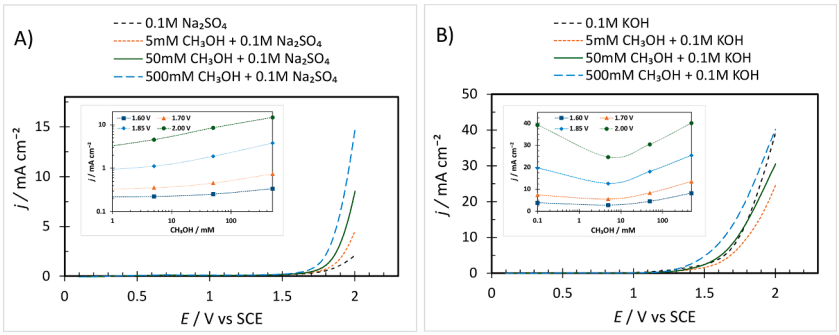

Fig. 1. Effect of methanol concentration (0, 5, 50, and 500 mM) on anodic oxidation in voltammetry, recorded at 0.1 V s^{-1} in the potential range 0–2.0 V vs SCE, at a BDD electrode in Na_2SO_4 (1A) and KOH (1B). Insets report the current density as a function of methanol concentration at selected fixed potentials (1.60, 1.70, 1.85, and 2.00 V vs SCE).

3. Results and discussion

3.1. Anodic oxidation of methanol at BDD

Cyclic voltammetry experiments were performed to investigate the anodic oxidation of methanol in aqueous solution at BDD using Na_2SO_4 or KOH as a supporting electrolyte (SE). Fig. 1A shows the cyclic voltammograms recorded in 0.1 M Na_2SO_4 in the absence and in the presence of increasing CH_3OH concentrations (5, 50 and 500 mM). In the absence of methanol, water oxidation (eqs. (4) and (5)) occurred at potentials higher than 1.8 V vs. SCE. Additionally, a very small oxidation current was observed at potentials close to 0.7 V, which slightly increased upon the addition of CH_3OH. More relevant, in the region of water decomposition, the current density (*j*) increased markedly in the presence of methanol (Fig. 1A). As shown in the inset of Fig. 1A, for a given potential, *j* increased with organic concentration. A similar behavior has been reported for the oxidation of various organics at BDD and, in particular, by Kapalka et al. [30] in the case of the methanol oxidation at BDD in 1 M $HClO_4$. These results clearly indicate that methanol oxidation at BDD occurs in the potential region associated with water decomposition, likely due to oxidation by means of hydroxyl radicals either adsorbed (eq. (6)) or in the homogeneous phase [30,31,33]. In particular, the group of Comninellis proposed that, in the case of methanol, the reaction between adsorbed $HO^{\bullet}$ and organics leads to a decrease of the surface coverage of hydroxyl radicals, thereby accelerating water oxidation [30].

When cyclic voltammetry was performed in 0.1 M KOH, water oxidation occurred at less positive potentials (Fig. 1B), due to the high pH which favors reactions (4) and (5). Upon the addition of methanol, a complex behavior was observed (Fig. 1B). Specifically, at methanol concentrations of 5 and 500 mM, a decrease and an increase of *j* in the region of water decomposition, respectively, were observed as compared to *j* values measured in the absence of methanol. At an intermediate methanol concentration of 50 mM, the presence of the alcohol caused a slight increase of *j* for $E < 1.8$ V followed by a decrease at more positive potentials. More specifically, as shown in the inset in Fig. 1B, at a fixed potential, the addition of 5 mM CH_3OH caused a decrease of *j*, whereas further increases in methanol concentration led to a progressive increase of *j*. A decrease of *j* was previously observed for other organics such as formic and maleic acids, and it was explained considering that such molecules can give rise to adsorption phenomena that can reduce the active sites available for water oxidation [28]. Hence, the behaviors shown in Fig. 1 may indicate that in KOH solutions methanol could be adsorbed onto BDD anode and could subsequently be directly oxidized in competition with water oxidation.

According to the literature, at BDD the direct oxidation of organics generally involves partial oxidation and does not give rise to CO_2 formation, while oxidation via hydroxyl radicals is less selective and leads also to total oxidation to CO_2 [22,23].

Table 1
Preliminary potentiostatic electrolyses focusing on MOR at BDD.[a].

Operative conditions	Average current density (mA cm^{-2})	Faradic efficiency (%)		
		FA	CO	CO_2
Na_2SO_4, $E = 2.0$V	5	28 - 32	3 - 5	16 – 20
KOH, $E = 1.8$ V	14	49 - 53	1 - 3	1 - 2
KOH, $E = 1.25$ V	0.6	58 - 62	n.d.	n.d.

[a] Potentiostatic electrolyses performed using a tin cathode and a BDD anode for 2 hours in a divided cell in aqueous solution. 0.5 M CH_3OH was present in the anolyte.

To gain further information on the anodic oxidation of methanol at BDD, some focused potentiostatic electrolyses were performed for 2 h using both KOH and Na_2SO_4 as SEs. An undivided cell equipped with a BDD anode and a Sn cathode was used. In the case of Na_2SO_4, experiments carried out at 2.0 V vs. SCE gave rise to an initial *j* of 6 mA cm^{-2} which gradually decreased to 4 mA cm^{-2}. FA was produced in the anodic compartment with a faradic efficiency (FE_{FA}) close to 30% (Table 1), showing that BDD can promote the conversion of methanol to FA. Part of methanol was also oxidized to CO and CO_2 with a faradic efficiency close to 4 and 18 %, respectively, as expected for an oxidation process by means of hydroxyl radicals. As expected, oxygen evolution due to water oxidation was also observed.

In the case of KOH, electrolyses were conducted at two different potentials (1.25 and 1.8 V vs. SCE). As reported in Table 1, in both cases, considerably higher FE_{FA} and very low faradic efficiencies in CO and CO_2 were obtained with respect to the electrolysis performed with Na_2SO_4. In particular, the highest FE_{FA}, which was close to 60 %, was achieved at 1.25 V, but the *j* was very low (< 1 mA cm^{-2}). Also, a significant production of oxygen was observed when KOH was used as SE.

Finally, the electrolyses carried out with Na_2SO_4 were repeated under the same operative conditions ($E = 2.0$ V vs. SCE) adding CO_2 in the cathodic compartment to evaluate FA production in both compartments. Interestingly, FA was produced in both compartments even if with very different FE_{FA} close to 70 and 30% in the catholyte and in the anolyte, respectively.

3.2. Effect of the nature of supporting electrolyte

It has been previously demonstrated that the nature of the SE significantly influences the $ERCO_2$ processes by various investigations [2]. However, the same level of attention was not previously given to the effect of SE on both cathodic and anodic processes of the paired electrosynthesis. Since the preliminary electrolyses reported in the previous section showed that the nature of SE can affect significantly also the

Table 2
Effect of the pH and of the SE on the paired process.[a]

Entry	SE	pH_{cat} (initial – final)	pH_{an} (initial – final)	$FE_{FA(cat)}$	$FE_{FA(an)}$
1	K_2SO_4	4.5 – 6.0	5.4 – 2.0	66	35
2	Na_2SO_4	4.7 – 6.0	6.5 – 2.0	72	32
3	KOH	6.9 – 7.1	13.2 – 12.6	49	34
4	Cs_2SO_4	4.3 – 5.7	4.8 – 1.7	70	27
5	$KHCO_3$	6.7 – 6.5	7.5 – 7.5	67	18

[a] Electrolyses performed using a tin cathode and a BDD anode for 2 hours in a divided cell with an aqueous solution of different SE (0.1 M) at 11 mA cm^{-2}; 0.5 M CH_3OH was present in the anolyte.

MOR process at BDD, we undertook a detailed investigation into the effects of the cationic and anionic components of the SE on both cathodic and anodic processes of the PEP to FA, using BDD and Sn as anode and cathode, respectively. The examined SEs (0.1 M) were K_2SO_4, Na_2SO_4, Cs_2SO_4, KOH, NaOH and $KHCO_3$. Amperostatic conditions were imposed in order to have the same current densities in all experiments. As shown in Table 2 and in Fig. 2, both the cation and the anion of the SE markedly affected the performance of the cathodic and anodic processes, albeit in a different mode. To specifically evaluate the influence of the anion, CO_2 and MeOH conversions into FA were analyzed using K_2SO_4, $KHCO_3$ and KOH, thereby maintaining the same cation. Notably, the nature of the anion strongly influenced the pH of the electrolytic solution (Table 2):

- in the case of K_2SO_4 (Table 2, entry 2), the initial pH of the catholyte was approximately 4.5 owing to the acidic nature of H_2CO_3 (eqs. (9)–(11)) [34,35], but increased up to 6.0 over time as cathodic reactions raised the pH; conversely, the anolyte initially exhibited a pH close to 5.4, which decreased substantially to quite acidic conditions due to anodic reactions (eqs. (2)–(5)) [2];

$$CO_{2(aq)} + H_2O \rightleftarrows H_2CO_{3(aq)} \left(K_e = 3.4\ 10^{-2}\right) \quad (9)$$

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^- \left(K_a = 4.5\ 10^{-7}\right) \quad (10)$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^- \left(K_a = 4.7\ 10^{-11}\right) \quad (11)$$

- when the strong base KOH was used as the SE, the anolyte became highly basic, whereas the catholyte remained close to neutral (pH ≈ 7; Table 2, entry 3), due to the reaction between KOH and CO_2, which gives rise to $KHCO_3$;
- $KHCO_3$ acts as a buffer, thus maintaining the pH close to neutrality in both compartments (Table 2, entry 5).

As shown in Fig. 2A and in Table 2, the nature of the anion exerted a pronounced influence on the anodic process. The production of FA (Fig. 2A) and the relative FE_{FA} (Table 2) at the anode followed the order $HCO_3^- << SO_4^{2-} \sim OH^-$. This trend is consistent with previous findings at various electrodes, where the MOR was shown to be favored under strongly basic conditions and in the presence of hydroxide ions (OH^-) [36]. However, our results demonstrate that, when using BDD anodes,

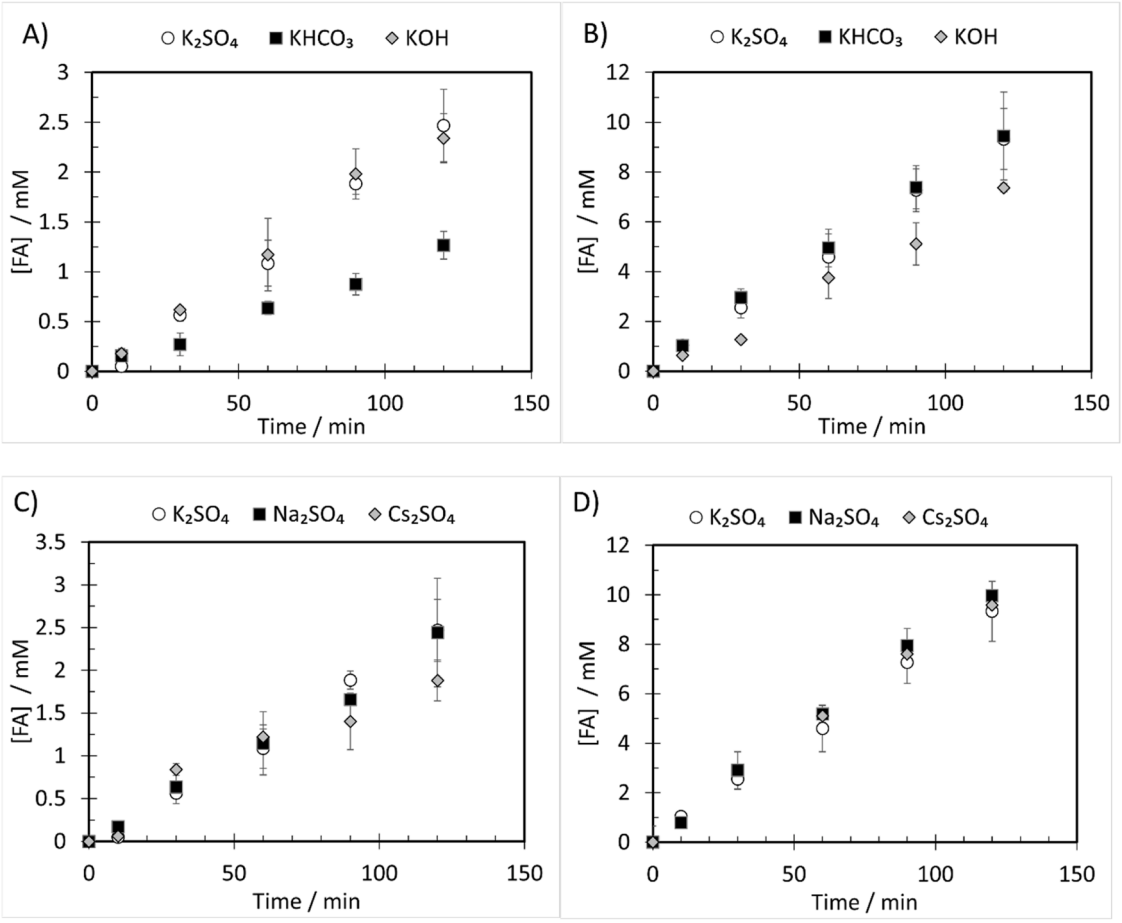

Fig. 2. Effect of the SE on the production of FA in the anodic (2A and 2C) and cathodic (2B and 2D) compartments. Fig. 2A and 2B report the effect of the anion while 2C and 2D show that of the cation. All electrolyses were performed at 11 mA cm^{-2} using a tin cathode and a BDD anode for 2 hours in a divided cell with an aqueous solution containing 0.1 M SE in both compartments and 0.5 M MeOH in the anolyte.

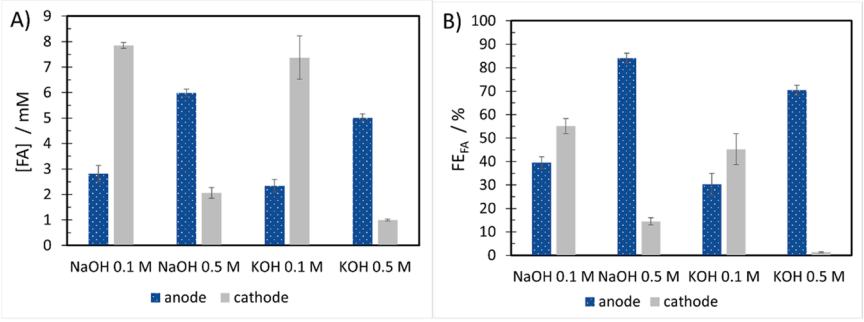

Fig. 3. Effect of the SE concentration on [FA] (3A) and FE_{FA} (3B) achieved at the end of the electrolyses for both anodic and cathodic processes. Electrolyses were performed at 11 mA cm^{-2} using a tin cathode and a BDD anode for 2 hours in a divided cell with an aqueous solution of NaOH or KOH in both compartments and 0.5 M MeOH in the anolyte.

comparable FA yields can also be achieved under mildly acidic conditions with K_2SO_4 as the SE.

As illustrated in Table 2 and Fig. 2B, the $ERCO_2$ exhibited a markedly different behavior. The lowest FA production and FE_{FA} were observed with KOH, while the highest occurred with $KHCO_3$ and K_2SO_4. This observation aligns with previous reports indicating that CO_2 conversion to FA is favored under slightly acidic conditions [32]. Moreover, the presence of HCO_3^- increased the local CO_2 concentration through the equilibria described by reactions (9) and (10).

Overall, as shown in Fig. 2A and 2B, K_2SO_4 provided favorable performance for both the anodic and cathodic processes.

To assess the effect of the cation in the SE, a series of electrolyses was carried out using K_2SO_4, Na_2SO_4 and Cs_2SO_4. As shown in Fig. 2C and 2D and in Table 2, the SE composition affected the two compartments differently:

- the cathodic conversion of CO_2 to FA was slightly enhanced when K^+ (Table 2, entry 1) was replaced by Na^+ or Cs^+ (Table 2, entries 2 and 4; Fig. 2D), although the effect was relatively minor; indeed, according to the literature, bigger metal alkali cations are expected to cause a thinner electrical double layer and a stronger electric field, thus favoring the $ERCO_2$ process [40];
- conversely, the anodic conversion of MeOH to FA was slightly lower in the presence of Cs^+ than K^+ and Na^+ (Table 2, compare entries 1, 2 and 4; Fig. 2C); it was previously found that the activities for alcohol oxidation at Pt in solutions containing Na^+ are lower than those in Cs^+ solutions. According to the authors, alkali cation effects on the surface oxidation result from the competitive interactions between the adsorption energy of oxygen-species and the binding energy of oxygen-species to cation [37].

For all these electrolyses, the main by-products of both anodic and cathodic processes were searched. The anodic process resulted in the generation of CO and CO_2, due to the partial and complete oxidation of methanol, and O_2 due to the parasitic anodic oxidation of water. In particular, the yield of MOR to CO was low for all SEs. Interestingly, however, the bicarbonate-based SE produced the highest amount of CO, with a FE close to 10%, compared to approximately 4–5% for the other SEs. The main by-products for the cathodic process were CO, which was generated for all adopted SEs with faradic efficiencies lower than 6%, and H_2 which was produced by the parasitic water reduction.

3.3. Effect of the SE concentration

According to the literature [36], MOR is favored by a high concentration of hydroxide ions. Therefore, some electrolyses were conducted using KOH and NaOH as SEs at concentrations of 0.1 and 0.5 M. For comparison, the effect of increasing the concentration of Na_2SO_4 was also evaluated.

An increase in the concentration of NaOH or KOH led to a slight rise in pH in both compartments. For NaOH and KOH, the final pH in the anodic solution reached approximately 12.3–12.5 and 12.8–13.5 for SE concentrations of 0.1 and 0.5 M, respectively, while in the cathodic solution the final pH values were about 7 and 8 for the same SE concentrations, due to the reaction between KOH or NaOH and CO_2, which gives rise to $KHCO_3$ or $NaHCO_3$, respectively.

Fig. 3 shows the final [FA] and FE detected for both $ERCO_2$ and MOR processes under the various experimental conditions. The following trends were observed for the anodic conversion of MeOH to FA:

I. for both KOH and NaOH, increasing the [SE] from 0.1 to 0.5 M caused a pronounced rise in [FA] in the anodic compartment (Fig. 3A) and a marked increase in the FE (Fig. 3B). For example, when [NaOH] was raised from 0.1 to 0.5 M, [FA] after 2 hours of electrolysis increased from 2.8 to 6.0 mM as FE rose from 40% to 84%;
II. NaOH yielded higher [FA] and FE values than KOH at both 0.1 and 0.5 M (Fig. 3A and 3B), indicating that under these conditions the Na^+ cation promotes FA formation at the anode;
III. for the sake of comparison, when the experiments were repeated with Na_2SO_4 as SE, a slight decrease in [FA] was observed by increasing [Na_2SO_4] from 0.1 to 0.5 M (data not shown), confirming that the key parameter governing MeOH-to-FA conversion is not the overall [SE] but rather the hydroxide ion concentration.

A different behavior was observed for the cathodic process. In this case, increasing the SE concentration (for both NaOH and KOH) led to a substantial decrease in [FA] in the solution (Fig. 3A) and a significant reduction in FE (Fig. 3B). Conversely, for Na_2SO_4, only a minor decrease in FA production was detected (data not shown) upon increasing the SE concentration.

3.4. Effect of methanol concentration

Two series of electrolyses were carried out at a BDD anode to investigate the influence of MeOH concentration (up to 1 M in both compartments) on both $ERCO_2$ and MOR. In all experiments, 0.1 M Na_2SO_4 was employed as the SE in the cathodic compartment. The anodic compartment contained either 0.1 M Na_2SO_4 or 0.5 M NaOH, depending on the experimental series.

It is noteworthy that the presence of MeOH enhances the solubility of CO_2, which may be beneficial for sustaining the process at high *j*. For example, the addition of 0.1 M MeOH is expected to increase CO_2 solubility by approximately 18% [38]. On the other hand, MeOH might affect the kinetics of CO_2 reduction by interacting with the tin surface thus modifying its catalytic activity for $ERCO_2$.

Pleasingly, as shown in Fig. 4, the addition of MeOH did not

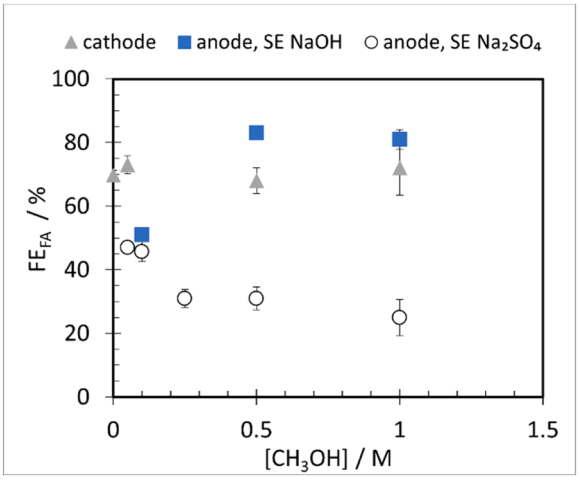

Fig. 4. Effect of the MeOH concentration on FE on the anodic and cathodic compartments. Electrolyses were performed at 11 mA cm^{-2} using a tin cathode and a BDD anode for 2 hours in a divided cell with an aqueous solution of 0.1 M Na_2SO_4 in the cathodic compartment and 0.1 M Na_2SO_4 or 0.5 M NaOH in the anodic one.

adversely affect the cathodic CO_2 reduction. Comparable FE ≈ 70% were obtained both in the absence of MeOH and in its presence at various concentrations. Conversely, the MeOH concentration had a pronounced effect on FA production in the anodic compartment, and two distinct behaviors were observed depending on the SE used:

- in NaOH electrolyte, increasing the MeOH concentration from 0.05 to 0.5 M led to a marked enhancement in FE from 51% to 83%. However, further increase in MeOH concentration to 1 M resulted in a slight decline in FE to 81%;
- when Na_2SO_4 was used as the SE in the anodic compartment, FEs of approximately 50% were recorded at low MeOH concentrations (0.05 and 0.1 M). In contrast, increasing MeOH concentration caused a pronounced drop in efficiency, reaching values near 25% at 1 M MeOH.

3.5. *Effect of the temperature*

Previous studies have demonstrated that both the $ERCO_2$ at tin cathodes and the MOR at copper-based anodes are significantly influenced by the temperature [16]. For example, it was reported that lowering the temperature enhanced the formation of FA at Sn cathodes, with the best performance observed at the lowest tested temperature of 3°C [39]. Conversely, Baessler et al. [20], found a positive effect of raising the temperature on FA production during the MOR under markedly different conditions, namely using a CuO-on-copper-foam anode in a KOH electrolyte.

In the present work, the temperature effect was examined by performing a series of electrolyses at 2, 6, 13, 24, and 35°C, employing 0.1 M Na_2SO_4 as SE in both anodic and cathodic compartments. Moreover, the effect of the temperature was evaluated also using NaOH 0.5 M in the

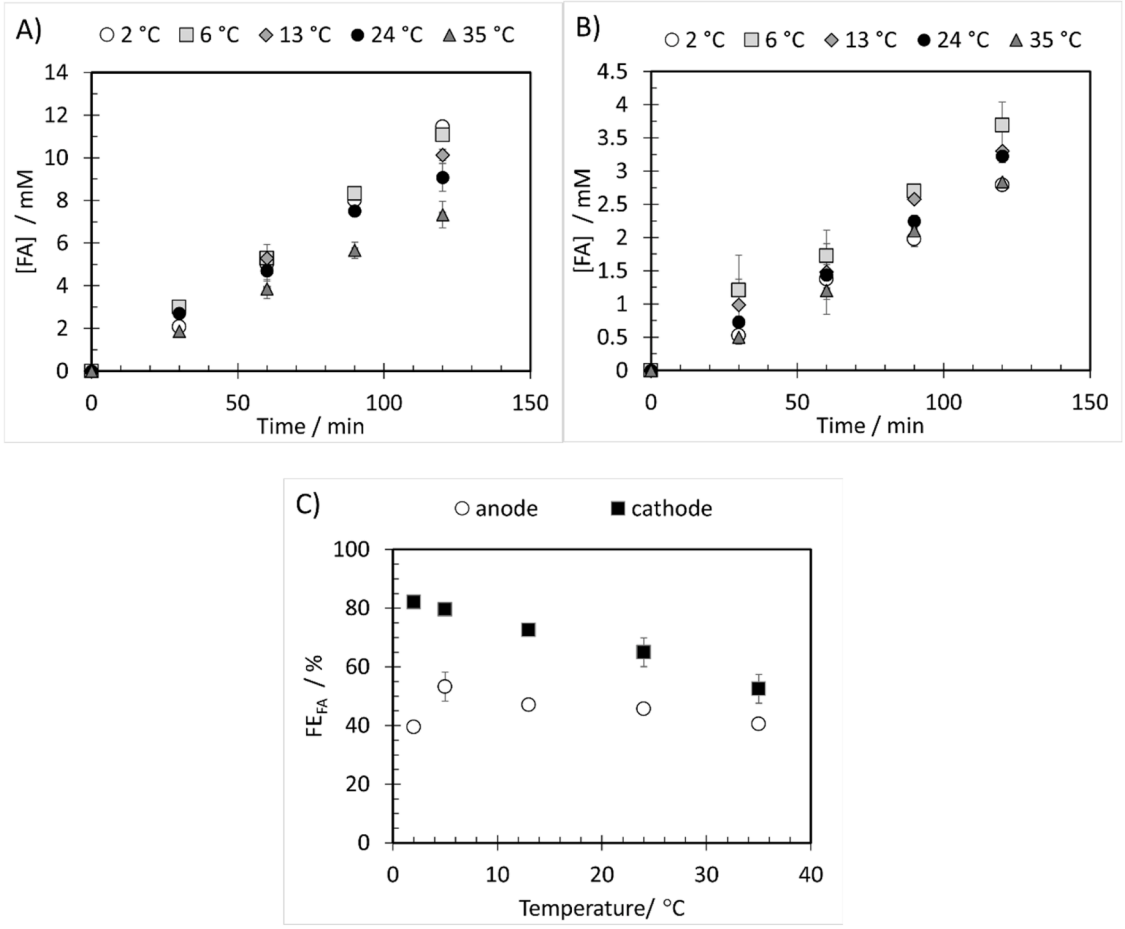

Fig. 5. Effect of the temperature on the production of FA in the cathodic (5A) and anodic (5B) compartments and the final FE_{FA} obtained in each compartment (5C). All electrolyses were performed at 11 mA cm^{-2} using a tin cathode and a BDD anode for 2 hours in a divided cell with an aqueous solution of 0.1 M Na_2SO_4 and 0.1 M MeOH in both compartments.

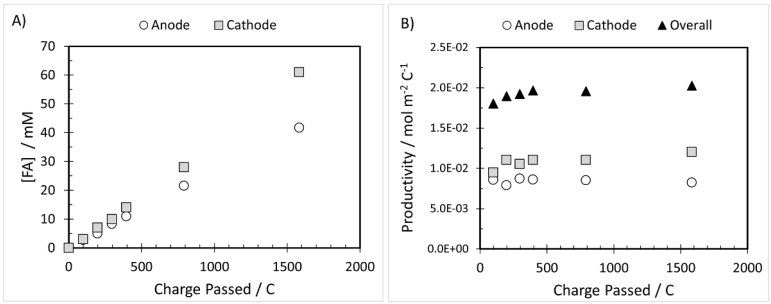

Fig. 6. Effect of the charge passed on [FA] (6A) and FA productivity (6B) achieved in the cathodic and anodic compartments. Fig. 6B reports also the overall productivity achieved in the cell. All electrolyses were performed at 22 mA cm^{-2} using a tin cathode and a BDD anode in a divided cell with an aqueous solution of 0.1 M Na_2SO_4 in the catholyte and 0.5 M NaOH and 0.5 M MeOH in the anolyte. $T = 23°C$.

anodic compartment performing a series of experiments at 6 and 24°C. As illustrated in Fig. 5A, the temperature exerted a pronounced influence on the cathodic production of FA. A decrease in temperature led to a substantial increase in FA formation: after 2 hours of electrolysis, the FA concentrations were 7.3, 9.1, 10.1, 11.1, and 11.5 mM at 35, 24, 13, 6, and 2°C, respectively. Accordingly, as shown in Fig. 5C, the FE increased from 53% at 35°C to 82% at 2°C.

The temperature also affected the anodic production of FA using Na_2SO_4 as SE (Fig. 5B). When the temperature was lowered from 35°C to 6°C, the FA concentration in the anolyte rose from 2.8 mM to 3.7 mM. However, a further reduction of temperature to 2°C resulted in a decline of FA production to 2.8 mM. As shown in Fig. 5C, the relationship between FE and temperature exhibited a maximum at 6°C, where FE reached approximately 53%.

In contrast to the remarkable temperature effect on MOR shown in Fig. 5, when 0.5 M NaOH and 0.5 M CH_3OH were used in the anolyte the effect of the temperature was quite small. Indeed, FE values close to 85 and 90% were observed at 24 and 6°C, respectively.

3.6. *Effect of charge passed*

The experiments described in the previous sections were conducted up to a total charge of approximately 200 C. To investigate the effect of the charge passed on the performances of cathodic and anodic routes, additional electrolysis tests were carried out up to 1600 C. These experiments were performed using 0.1 M Na_2SO_4 and 0.5 M NaOH as SEs in the cathodic and anodic compartments, respectively. In addition, 0.5 M CH_3OH was present in the anolyte. Fig. 6A and 6B report the [FA] and FA productivity as a function of the charge passed, respectively.

As shown in Fig. 6A, the plot of [FA] vs. charge passed exhibited an almost linear trend in both anodic and cathodic compartments, indicating a quite good stability of the system over adopted electrolysis duration. Consistently, the FA productivity, calculated as the number of FA moles produced per unit electrode area and per unit charge passed (moles m^{-2} C^{-1}), presented almost constant values for both compartments. For the anodic process, an FA productivity close to 8.6×10^{-3} moles m^{-2} C^{-1} was recorded corresponding to faradic efficiencies close to 70 %. In the case of the cathodic process, a higher FA productivity close to 1.2×10^{-2} moles m^{-2} C^{-1} was observed, due to the lower number of electrons required for the electroreduction of CO_2 to FA compared to those involved in the MOR, partially compensated by the slightly lower FE values. Overall, the electrochemical cell provided an almost constant total FA productivity close to 2×10^{-2} moles m^{-2} C^{-1} over the investigated charge passed (Fig. 6B).

4. Conclusions

This work demonstrates the feasibility of the paired electrochemical synthesis of FA through the simultaneous cathodic reduction of CO_2 and anodic oxidation of MeOH using a tin cathode and, for the first time, a BDD anode, respectively. The use of BDD provides interesting features such as higher FEs with respect to various anodes largely investigated in the literature, such as Pt, and good stability in various environments, which allows to work both in basic and neutral media. This last aspect underlines the superiority of BDD than anodes such as Ni nanoparticles that provide very high FE but can work only in basic conditions. The study shows that the BDD anode enables high FEs for MeOH oxidation under properly selected conditions and confirms that the tin cathode ensures efficient CO_2 reduction to FA. The nature of the supporting electrolyte proved particularly important:

- in the catholyte, the use of a 0.1 M alkali sulfate electrolyte provided the most favourable results;
- in the anolyte, similar results were obtained using 0.1 M SE with NaOH, KOH, Na_2SO_4 or K_2SO_4; however, when the SE concentration was increased to 0.5 M, both NaOH and KOH significantly outperformed the other tested electrolytes, leading to notably higher FA yields in the paired configuration.

The reaction temperature also played a decisive role. Operating at low temperatures (e.g., 6°C) markedly enhanced FA production at both the cathode and the anode. Overall, the combined analysis of electrolyte composition, concentration, and temperature demonstrates that the paired FA synthesis can achieve high efficiency when properly optimized. A quite good stability of the system was observed over 1600 C.

To better evaluate the potential use of BDD anodes for the synthesis of FA by PEP on an applicative scale, further studies will be necessary involving (i) a detailed comparison of the performance of BDD with those of conventional anodes, (ii) the study of the performance of the system at high current densities in flow-cells equipped with gas diffusion cathodes and/or in pressurized systems, (iii) the use of undivided cells and (iv) the evaluation of the process from an economic point of view.

CRediT authorship contribution statement

Paola Meli: Investigation, Data curation. **Alessandro Galia:** Funding acquisition. **Abdirisak Ahmed Isse:** Writing – review & editing, Supervision, Funding acquisition. **Roberta Panepinto:** Investigation, Data curation. **Federica Proietto:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Onofrio Scialdone:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

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

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Data availability

Data will be made available on request.

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