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Continuous electrochemical reduction of carbon dioxide into formate using a tin cathode: Comparison with lead cathode

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ABSTRACT

Electrochemical reduction has been pointed out as a promising method for CO_2 valorisation into useful chemicals. This paper studies the influence of key variables on the performance of an experimental system for continuous electro-reduction of CO_2 to formate, when a tin plate is used as working electrode. Particular emphasis is placed on comparing the performance of Sn and Pb as cathodes. As was previously found with Pb, the influence of current density ("j") using Sn was particularly noteworthy, and when j was raised up to a limit value of 8.5 mA cm^{-2}, important increases of the rate of formate production were observed at the expense of lowering the Faradaic efficiency. However, unlike what was found with Pb, the performance using Sn improved when the electrolyte flow rate/electrode area ratio was increased within the range studied (0.57–2.3 mL min^{-1} cm^{-2}). In this way, the use of Sn as cathode allowed achieving rates of formate production that were 25% higher than the maximum rates obtained with Pb, together with Faradaic efficiencies close to 70%, which were 15 points higher than those with Pb. These results reinforce the interest in Sn as electrode material in the electro-reduction of CO_2 to formate.

Keywords: Carbon dioxide; Valorisation; Electrochemical reduction; Formate; Continuous filter-press cell; Sn cathode

Introduction

Fossil fuels (i.e. oil, coal and natural gas) represented 81.1% of the total primary energy supply in the world in 2010, while renewable energies only accounted for 13.2% (IEA, 2011). Although the final objective for many countries is to phase out fossil fuels in heat and power production as well as in the transport sector (Toftegaard et al., 2010), prospects for the future indicate that the shift to renewable energy sources is slow and that the world energy supply will still depend on fossil fuels in the next decades.

The anthropogenic emissions of carbon dioxide (CO_2), which is the most significant greenhouse gas, are a major cause of global climate change (Figueroa et al., 2008), and they represent a complex challenge that needs to be tackled. Among the different alternatives that are being considered, the so-called "CO_2 valorisation" or "CO_2 chemical recycling" to convert CO_2 into useful and valuable products such as fuels or other derived hydrocarbons (Arakawa et al., 2001; Jiang et al., 2010; Mikkelsen et al., 2010; Quadrelli et al., 2011; Yu et al., 2008) appears as an innovative and attractive option, which has been regarded as a feasible and powerful new approach that is entering the stage of gradual practical implementation (Olah et al., 2009, 2011). Particularly, electrochemical valorisation of CO_2 is receiving increasing attention over the last years. Several papers can be found in the literature that have reviewed different efforts in the study of CO_2 electro-reduction and have discussed mechanistic aspects and reaction pathways (Chaplin and Wragg, 2003; Gattrell et al., 2006; Jitaru et al., 1997; Jitaru, 2007; Lee et al., 2009; Spinner et al., 2012; Sánchez-Sánchez et al., 2001; Whipple and Kenis, 2010).

Valorisation of CO_2 by electrochemical reduction is based on the supply of electrical energy to establish a potential between two electrodes in order to allow CO_2 to be converted into reduced forms. Different authors have suggested that the electrochemical valorisation of CO_2 may be an excellent way

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of storing intermittent and unpredictable renewable energy, which can be used for supplying the electricity required for this process (Agarwal et al., 2011; Chen and Kanan, 2012; Narayanan et al., 2011; Olah et al., 2011; Prakash et al., 2013; Wang et al., 2013; Whipple et al., 2010). A negative public opinion to CO_2 storage, which has already been detected recently in the lack of social acceptance of some projects for storing captured CO_2, may hamper its implementation (Ashworth et al., 2012; Terwel and Daamen, 2012; Terwel et al., 2012; Upham and Roberts, 2011) and therefore may increase the interest in finding ways of converting captured CO_2 into useful products. Particularly, coupled to a renewable energy source such as wind or solar, electrochemical processes for CO_2 conversion could generate carbon neutral fuels or industrial chemicals that are conventionally derived from petroleum (Kuhl et al., 2012), and at the same time, could also allow the storage of electrical energy in chemical forms, which has been remarked as a key aspect for levelling the output from intermittent electricity sources such as wind and solar (Whipple and Kenis, 2010). Since electricity is difficult to store on a large scale, its production has to closely follow the demand and to adapt to fluctuations; however, renewable energies such as solar and wind are intermittent and not able to follow closely the demand (i.e. solar energy cannot be produced during the night or with cloudy weather, while wind does not blow constantly), so storage of electricity to balance fluctuations in demand and production cycles is considered to be essential for the use of renewable energies on a large scale (Olah et al., 2011; Prakash et al., 2013). In this way, it has been highlighted that if the electrochemical reduction of CO_2 to liquid chemical compounds could be made with high efficiencies, it could become a sustainable approach in the future for the production of liquid fuels, providing a high energy density means of storing renewable electricity as chemical energy (Gattrell et al., 2006; Kuhl et al., 2012; Narayanan et al., 2011; Olah et al., 2011; Prakash et al., 2013; Whipple et al., 2010).

In the electro-reduction of CO_2, the type of products, as well as the yield in which they can be obtained, are strongly dependent on different factors, emphasising the nature and form of the material used as cathode, the medium where the reaction occurs or the conditions of pressure and temperature (Hori et al., 1994; Jitaru et al., 1997; Jitaru, 2007; Sánchez-Sánchez et al., 2001). Among the number of useful products into which CO_2 can be electrochemically reduced, conversion to formic acid/formate appears to have the best chance for the practical development of technical and economically viable processes (Oloman and Li, 2008). Apart from its different traditional industrial uses, including textile finishing or additive in animal feeds (Kirk-Othmer, 2004), a growing demand for formic acid in pharmaceutical synthesis and in paper and pulp production has been reported (Innocent et al., 2009). Furthermore, formic acid has been pointed out as one of the most promising candidate fuels for fuel cells (Rees and Compton, 2011; Yu and Pickup, 2008) and recently has been proposed as an optimal hydrogen carrier (Grasemann and Laurenczy, 2012; Prakash et al., 2013). However, formate/formic acid is currently mainly produced by the oxidation of hydrocarbons or by thermo-chemical processes based on the carbonylation of methanol or sodium hydroxide (Kirk-Othmer, 2004), which have negative environmental impacts (Li and Oloman, 2006) and are relatively expensive production processes (Agarwal et al., 2011).

As a consequence, the study of the electrochemical reduction of CO_2 to formate has attracted renewed and growing interest over the last years. Some studies have used fixed-bed reactors (Köleli et al., 2003; Köleli and Balun, 2004; Kwon and Lee, 2010) or divided H-type cells (Chen and Kanan, 2012; Kaneco et al., 1998, 1999; Li et al., 2012). Nevertheless, several works in the literature have been focussed on parallel-plate or filter-press flow-by type cells (Agarwal et al., 2011; Akahori et al., 2004; Alvarez-Guerra et al., 2012; Innocent et al., 2009; Li and Oloman, 2005, 2006, 2007; Machunda et al., 2010, 2011; Narayanan et al., 2011; Subramanian et al., 2007; Whipple et al., 2010), under different working conditions and cathodes of very different nature, such as indium-impregnated lead wire (Akahori et al., 2004), lead-plated stainless steel woven mesh (Subramanian et al., 2007), tinned-copper mesh (Li and Oloman, 2005, 2006), tin particles (shots and granules) (Li and Oloman, 2007), lead plates (Alvarez-Guerra et al., 2012; Innocent et al., 2009), or metal catalysts (such as indium, Narayanan et al., 2011; lead, Machunda et al., 2010; or tin, Agarwal et al., 2011; Machunda et al., 2011; Whipple et al., 2010) electrodeposited on different substrates. Apart from very recent investigations focussed on new gas diffusion electrodes (Li et al., 2012; Prakash et al., 2013), the CO_2 electrochemical valorisation to formate in continuous mode has been particularly studied in several works (Agarwal et al., 2011; Alvarez-Guerra et al., 2012; Li and Oloman, 2005, 2006, 2007; Subramanian et al., 2007), revealing the growing interest in this type of approach, but at the same time, emphasising that despite its great potential, there is the need for carrying on obtaining experimental evidence to guide the research efforts for developing and improving these processes.

Following previous studies of our research group using lead cathode (Alvarez-Guerra et al., 2012), the aim of this work is to analyse the influence of key variables like the current density and the electrolyte flow rate on the performance of an experimental system for continuous electro-reduction of CO_2 to formate, when a tin plate is used as working electrode in a filter-press electrochemical reactor. Special emphasis will be placed on comparing the performance of Sn plates with that of Pb plates previously reported (Alvarez-Guerra et al., 2012), and for this reason, the same approach was followed to carry out the analysis with Sn that will be presented in this paper, i.e. a 2^2 factorial design of experiments at different levels of current density and electrolyte flow rate, followed by subsequent more detailed studies of the influence of each of these variables on the performance of the process. These types of studies will allow the description of the system behaviour and can serve as a reference for the assessment of future advances.

Methods

In this work, the experimental laboratory system and operating conditions were the same as in our previous study using lead cathode (Alvarez-Guerra et al., 2012), with the only difference of using a tin plate (99.9% Sn, Amat Metalplast SA) as cathode. Details about the elements of the experimental set-up and about the methodology followed to carry out the experiments can be found in our previous work (Alvarez-Guerra et al., 2012). Briefly, the experimental laboratory system, whose core is a filter-press or parallel-plate type electrochemical cell (Micro Flow Cell, ElectroCell A/S), is represented in Fig. 1. A Nafion 117 cation-exchange membrane divided the cell in two separated anodic and cathodic compartments. In this study, the working electrode was a tin plate and a Dimensionally Stable Anode DSA/O_2 plate (Ir-MMO