On the modelling of multidisciplinary electrochemical systems with application on the electrochemical conversion of CO_2 to formate/formic acid

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ABSTRACT

This paper presents a model-based approach on the analysis of complex multidisciplinary electrochemical processes, with implementation on a reactor for the electrochemical conversion of CO_2 to formate/formic acid. The process is regarded as a system of interacting physical and electrochemical mechanisms. A process model is developed by combining individual mathematical sub-models of the mechanisms, organised at groups of compartments following the physical process structure. This approach results in a generic reconfigurable model that can be used as a part of integrated systems, and to test design modifications. The approach is demonstrated on an electrochemical cell, where CO_2 is converted to formate/formic acid. The model captures the molar transportation under electric field, the two-phase flow effects, and the key electrochemical reactions. The model is calibrated and validated against experimental data obtained from a continuous flow cell. The key parameters affecting the process performance are discussed through scale-up analysis.

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1. Introduction

CO_2 conversion and utilization have gained attention in the industry due to the capability of turning harmful emissions to valuable chemical feedstock, like formic acid, methanol, ethylene, polymers and inorganic minerals. There is a wide research portfolio on CO_2 conversion processes, however, their technical feasibility depends on the process economics and scale-up capability (Jhong et al., 2013).

Formic acid can be produced at high Faradaic efficiency (80–90%) on different metal catalysts at high over-potentials for H_2 production. Experimental studies in literature describe the impact of different electrode catalysts on the conversion performance, such as copper (Gupta et al., 2006; Hinogami et al., 2012), and tin and tin oxides (Chen and Kanan, 2012). Particularly, Sn has shown promise as a very high Faradaic efficiency catalyst for electrochem-

ical Reduction of CO_2. Using Sn as the base catalyst a chemical reactor to convert CO_2 to Formate/Formic Acid (ECFORM) ECFORM as a continuous process was developed by DNV GL since 2008 (Agarwal et al., 2012, 2011; Hill et al., 2011; Sridhar and Hill, 2011; Sridhar et al., 2010; Zhai et al., 2010). In this reactor, conversion of CO_2 takes place in an electrochemical reactor under an applied external voltage as the driving force, supplied by conventional or renewable power sources. ECFORM was demonstrated on experimental and semi-pilot (about 1 kg per day CO_2 conversion) scale powered by solar panels in a mobile trailer (Sridhar and Hill, 2011; Agarwal et al., 2012). Yet, the prediction of the ECFORM performance at variant conditions and larger scales is necessary to assess the process viability at industrial scale. In this respect, mathematical and computer-based tools for experiment design can enable the efficient testing of process modifications (electrodes, chemicals, etc.) and performance improvements at reduced experimental costs.

Modelling and simulation techniques can complement experimental work to cost-effectively explore the design space, providing insight on the process mechanisms and revealing their influence on the overall performance. Various studies in literature implement mathematical modelling on the purpose of understanding the interaction between transport and electrochemical

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Nomenclature

Latin characters

C	Molar concentration mole/m^3
D	Diffusion coefficient m^2/s
D_{corr}	Dispersion correction
d_H	Hydraulic diameter m
e	Relative error
F	Faradaic constant C/mole
f	Fanning factor
$\dot{G}$	Molar flux per volume mole/(m^3 s)
g	Gravity m/s^2
H	Cell height m
I	Current A
i	Current density A/m^2
i_0	Exchange current density A/m^2
k	Kinetic constant, units depend on the reaction, as follows: (I) forward & backward: mole/m^3 (II) forward: m^3/mole, backward: – (III) forward & backward: – (IV) forward & backward: – (V) forward: –, backward: m^3/mole
L	Cell length m
MSE	Mean squared error units depend on measured variable
N	Number of species
$\dot{N}$	Flux mole/(m^2 s)
n	Molar holdup mole/m^3
$\dot{n}$	Molar flowrate mole/s
P	Pressure Pa
R	Rate of consumption mole/(m^3 s)
r	Reaction rate mole/(m^3 s)
t	Time s
u	Mobility mol m^2/(s.V.C)
V	Voltage V
v	Velocity m/s
W	Cell width m
z	Charge

Greek characters

α	Tafel slope V
β	Calibration parameter m^2/s
δ	Drift-flux velocity factor
ε	Void fraction m^{3}gas/m^3 cell
λ	Mass transport coefficient m/s
ϑ	Stoichiometry coefficient
κ	Conductivity S/m
ρ	Mass density kg/m^3
ρ_n	Molar density mole/m^3
σ	Surface tension N/m
τ	Dispersion correction coefficient
Φ_0	Zero overpotential V
Φ	Potential V

Subscripts

A	Anode
C	Cathode
G	Gas phase
GL	Gas-to-Liquid
GS	Gas supply chamber
I-IV	Reaction indexes
L	Liquid phase
M	Mean
m	Membrane
mig	Migration
s	Superficial
TOT	Total
w	Wall

Superscripts

b	Backward
f	Forward
IN	Inlet

phenomena. The majority of studies is however process-specific or focus on the modelling approaches of individual mechanisms of the conversion process. In Byrne (2001), a mathematical model for chlorate and chlor-alkali cells was presented and compared against experimental data. The modelled mechanisms included two-dimensional single-phase flow, molar transport due to migration and diffusion, and electroneutrality. Single cell chamber geometry was considered, with the anolyte and the catholyte having no membrane separation. Bazant et al. (2005) analyzed the mechanisms that affect the current-voltage correlations using the Butler-Volmer kinetics to describe the cell potential boundary conditions. In Li and Oloman (2007), the experimental and model-based analysis of two trickle-bed reactors for the electro-reduction of CO_2 to potassium formate was performed under pure CO_2 gas feed conditions. Both reactors used cation membrane separators and operated in continuous flow conditions. The reactor model implemented a plug-flow approach and used Tafel kinetics to describe the conversion of CO_2 to formate. The model was verified against experimental data showing good fidelity over a range of operating conditions. The verified model was used to analyse the process at various scales and operating conditions, including different catholyte concentration and gas flow rate. In Rode et al. (2008), a mathematical model was presented for an electro-organic synthesis reactor characterised by three consecutive oxidation steps. The model was based on a system of plug-flow differential mass balance equations along the reactor height, Tafel-type rate laws for the electrochemical reaction kinetics and Newton-type laws for the mass transfer. The model captured the species concentration distribution in the bulk, allowing optimising the process with regards to the conversion efficiency. The process performance was investigated by adjusting three independent dimensionless parameters: a Wagner-like number, the number of transfer units, and a dimensionless current. A two-dimensional, dynamic model of a flat-plate electrode structure cell was shown by Chang (2009). The model captured the interaction between transport phenomena, thermodynamics and kinetics, but considered only the liquid cell phases. In Nakajo et al. (2011), a model was presented of the membrane electrode assembly of solid oxide fuel cells, following a generic modelling approach for the exchange current density at the anolyte/electrolyte interface. In particular, the proposed current density function accounted for the effect of the variation of the hydrogen and proton concentration close to the anode. In Wu et al. (2015), a steady-state isothermal model of a microfluidic cell that reduces CO_2 to CO was presented. The model mainly captured the mass transport at the gas and liquid phases, reaction kinetics and electrochemistry. The model was calibrated and validated against data obtained from experiments and showed good agreement with the experimental results.

This paper presents a phenomenological mathematical model of multi-compartment electrochemical cells and its implementation on the ECFORM process. The objective is to develop a generic foundation for model-based process analysis, variant design and scale-up testing, and in-depth understanding of the process phenomena. Our approach builds on past works on the modelling of