Solid State Ionics 231 (2013) 58–62

Contents lists available at SciVerse ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Electrochemical promotion of catalytic reactions: Thermodynamic analysis and calculation of the limits in Faradaic Efficiency

Ioannis Garagounis, Vasileios Kyriakou, Michael Stoukides *

Department of Chemical Engineering, Aristotle University, Thessaloniki, Greece
Chemical Process Engineering Research Institute, Thermi-Thessaloniki, Greece

ARTICLE INFO

Article history:
Received 4 May 2012
Received in revised form 7 September 2012
Accepted 19 October 2012
Available online 25 November 2012

Keywords:
NEMCA
Ammonia synthesis
Faradaic Efficiency limits

ABSTRACT

In the past three decades, more than 70 catalytic systems have been reported to exhibit the NEMCA phenomenon (Non-Faradaic Electrochemical Modification of Catalytic Activity). NEMCA has been observed in O^{2-}, Na^+, K^+, Pb^{2+} and H^+ conductors. As opposed to catalytic oxidations, however, in which dramatic increases in catalytic reaction rates have been observed, hydrogenation reactions exhibited weak NEMCA characteristics. The maximum Faradaic Efficiency (Λ) that can be obtained in a reaction with limited equilibrium conversion was calculated using a thermodynamic analysis. The values of Λ predicted by the present analysis are compared to those obtained experimentally during the reaction of NH_3 synthesis in a H^+ cell.

1. Introduction

Solid electrolytes have been used in the construction of solid electrolyte cell-reactors (SECRs) in which heterogeneous catalytic reactions were studied. A typical configuration of an SECR is shown in Fig. 1A. In this particular SECR, the solid electrolyte is an oxygen ion (O^{2-}) conductor and the reaction under study is the oxidation of compound A:

$$A + nO_2 <==> mB. \tag{1}$$

The cell consists of a dense solid electrolyte membrane and two porous electrodes, deposited on the two sides of the membrane. When the circuit is open and gaseous O_2 is fed in together with reactant A, the SECR behaves as a regular catalytic reactor. When the circuit is closed and either a constant voltage (potentiostatic operation) or a constant current (galvanostatic operation) is applied, the cell can additionally function as an electrochemical oxygen “pump”. For a pure O^{2-} conductor, the current, I, corresponds to I/4F moles of oxygen per second transported through the solid electrolyte. If r_o and r are the open- and closed-circuit reaction rates respectively (expressed in moles of oxygen/s), one can easily calculate the Faradaic Efficiency, Λ, and the rate enhancement factor, ρ. These two dimensionless numbers are defined as:

$$\Lambda = \Delta r/(I/4F) = (r - r_o)/(I/4F) \tag{2}$$

and

$$\rho = r/r_o \tag{3}$$

If $\Lambda = 1$, the effect is Faradaic, i.e. the increase in reaction rate equals the rate of ion transport through the electrolyte. In 1981, it was reported [1] that the oxidation of ethylene on Ag exhibited a strong non-Faradaic effect, i.e. Λ could exceed unity. Since then, the phenomenon of Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA), also called Electrochemical Promotion of Catalysis (EPOC), has been observed in numerous catalytic reaction systems [2–4]. Not only O^{2-}, but also Na^+, $K^{+-}$and Pb^{2+} conductors have been used. Moreover, after their discovery by the group of Iwahara [5], high temperature proton (H^+) conductors were used to study catalytic hydro- and dehydrogenation reactions [2–4,6]. In that case, the H^+ conducting SECR of Fig. 1B was used.

Ammonia synthesis is a hydrogenation reaction of great industrial importance. The Haber–Bosch process, the dominant process for its production, was developed at the beginning of the 20th century and involves the reaction of gaseous N_2 and H_2 on an Fe-based catalyst at high pressures [7]. Even from early studies, it was realized that the conversion is limited by thermodynamics. The number of moles decreases with reaction and at a given T and P, the gas volume decreases as well. Hence, an increase in pressure will increase the equilibrium conversion. The reaction is exothermic (−109 kJ/mol at 500 °C) and therefore the conversion decreases with temperature. In order, however, to achieve industrially acceptable reaction rates, the reaction temperature must be high. The trade-off solution is to operate at temperatures in the range of 430 to 480 °C, at which the equilibrium conversion is in the order of 10 to 15% [7].

---

* Corresponding author at: Department of Chemical Engineering, University Box 1517, Thessaloniki 54124, Greece. Tel.: +30 2310 996165; fax: +30 2310 996145.
E-mail address: stoukidi@cperi.certh.gr (M. Stoukides).

0167-2738/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ssi.2012.10.019

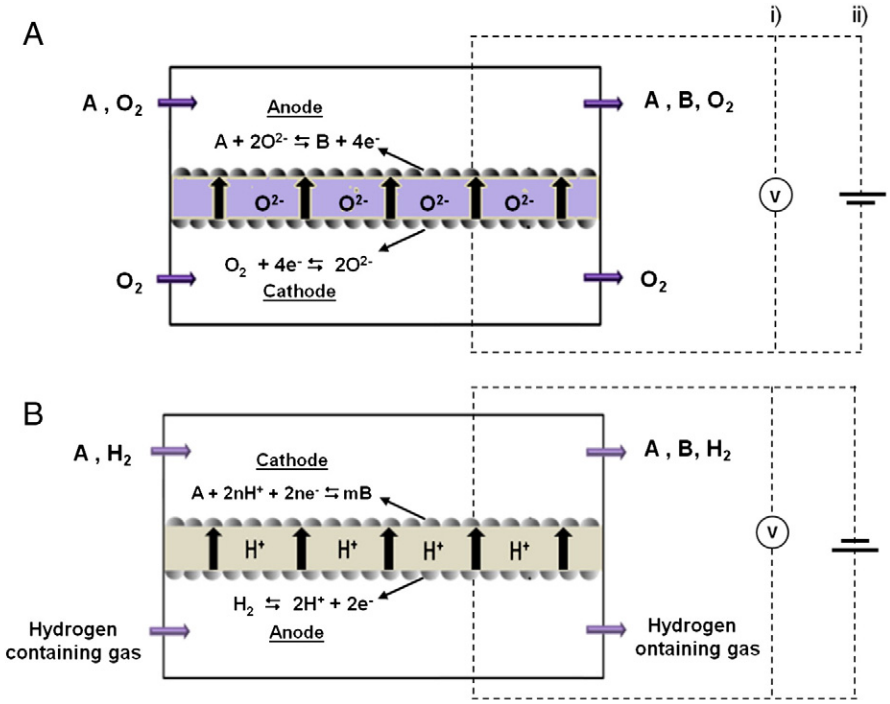

Fig. 1. A: Configuration of an oxygen ion-conducting solid-electrolyte cell. (i) open-circuit mode, and (ii) "pumping" mode. B: Schematic diagram of a proton (H^+) conducting cell reactor.

In the last 90 years, the search for more effective catalysts allowed operation at lower temperatures and pressures. Also, parallel to catalyst optimization, various alternative processes have been proposed including the electrochemical synthesis in SECRs [6,8–18]. The reaction was first studied by Marnellos et al. in a H^+ SECR on Pd electrodes [9,11]. A weak NEMCA effect was observed with Λ values remaining lower than 2.0. Yiokari et al. used a single-chamber reactor and studied the reaction on a commercial Fe catalyst [10]. Upon "pumping" H^+ to the catalyst surface, the reaction rate could increase by as much as 1300% ($\rho = 14$).

In general, as opposed to catalytic oxidation reactions, in which ρ values as high as 1400 and Λ values as high as 3×10^5 were reported [2,3], hydrogenation reactions studied in H^+ SECRs exhibited weak NEMCA characteristics. Although not explicitly stated, it was assumed that in order for Λ to attain values higher than 1.0 in a reaction with limited equilibrium conversion (such as NH_3 synthesis), the H^+ SECR should operate at conversions well below those predicted by thermodynamic equilibrium [10]. The phenomenon of electrochemical promotion, on the other hand, is the enhancement of catalytic activity, i.e. it refers to catalytic reaction kinetics. Hence, it is not clear why reactions with limited equilibrium conversion could not exhibit NEMCA.

In this communication, a thermodynamic analysis of NEMCA for reactions with limited equilibrium conversion is presented. The maximum value of Λ that can be achieved in this type of reactions is discussed. Ammonia synthesis in a H^+ SECR is used as a model system.

2. Open-circuit operation of the SECR

Assume that the H^+ SECR of Fig. 2A operates under open-circuit, i.e. protons are "pumped" neither to nor from the working electrode (catalyst). As already mentioned, if gaseous H_2 and N_2 are fed in together, the SECR behaves as a regular catalytic reactor. The steady state has been reached and the reactor operates at constant temperature T and at atmospheric total pressure. A stoichiometric mixture of H_2 and N_2 is introduced. The inlet molar flowrates are $N_1 = 100$ μmol N_2/s and $N_2 = 300$ μmol H_2/s. The reaction of NH_3 synthesis takes place:

$$3/2H_2 + 1/2N_2 <==> NH_3. \tag{4}$$

If the SECR has infinite length, the gas composition at the reactor exit can be calculated considering reaction (4) to be in a thermodynamic equilibrium. In that case, the reaction equilibrium constant K will be equal to:

$$K = \left(\alpha_{NH_3}/\alpha_{N_2}\right)^{0.5}\left(\alpha_{H_2}\right)^{1.5} \tag{5}$$

where α_{H_2}, α_{N_2} and α_{NH_3} are the thermodynamic activities of H_2, N_2 and NH_3 respectively. Assuming ideal gas behavior, activities can be replaced by partial pressures:

$$K = \left(P_{NH_3}\right)/\left(P_{N_2}\right)^{0.5}\left(P_{H_2}\right)^{1.5}. \tag{6}$$

In practice, the "infinite length" requirement is met either when a very active catalyst is used or, when the inlet flowrate is extremely low (or equivalently, the residence time of the gasses in the reactor is extremely long).

As an example, we assume that the rate of NH_3 formation is $r_{2a} = 6$ μmol NH_3/s. Then, the exit molar flowrates of H_2 and N_2 will be 291 μmol H_2/s and 97 μmol N_2/s, respectively. Eq. (6) can be used to calculate the equilibrium constant K:

$$K = (6/394)/(97/394)^{0.5}(291/394)^{1.5} = 0.0482 \tag{7}$$

which corresponds to a reaction temperature, $T = 573$ K [19,20]. The ammonia content at the reactor exit will be: $6/394 = 0.0152$ (1.5%).

Fig. 2B shows again another H^+ SECR which differs from that of Fig. 2A only in that the "infinite length" requirement is not met; the inlet flowrate is such that the exit composition is considerably lower than that predicted by thermodynamic equilibrium. Again, the inlet stream consists of 100 μmol N_2/s (N_1) and 300 μmol H_2/s