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NEMCA—From discovery to technology

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ABSTRACT

Serious research efforts of the last decades resulted in a profound understanding of the NEMCA effect and its demonstration in many reactions and electrolyte systems. Unfortunately, NEMCA has not been commercially applied yet. Reasons for the still missing commercial application are discussed in the paper. Furthermore, potential bottlenecks for industrial applications are identified and research directions indicated, which may open long-term opportunities for NEMCA applications.

1. Introduction

NEMCA (non-Faradaic-modification-of-catalytic-activity), discovered in the early 80s by Stoukides and Vayenas, is a special type of catalysis in which catalyst properties are purposely modified by applying an electrical field [1a]. At this time the observed non-Faradaic behaviour was considered as a peculiarity of the specific catalytic system (ethylene epoxidation on Ag) and was related to subsurface silver oxide. The identification of NEMCA as a new electrochemically induced catalytic effect was first reported in 1988 [1b]. The electrode of an electrochemical cell is thereby used as catalyst for two simultaneously occurring processes—a chemical and an electrochemical one. The major part of the yield is achieved by the chemical reaction pathway, which can include a heterogeneous catalytical reaction. This is the non-Faradaic part of the yield. The superimposed electrochemical reaction is actually used to control and improve the catalytic properties of the catalyst (electrode) surface. The by-product of this electrochemical reaction pathway is the Faradaic part of the overall yield. Only a minor part of the yield is generated through that electrochemical pathway (Faradaic mode). Obviously, NEMCA combines different features common to heterogeneous catalysis and technologies based on electrochemical polarisation (Fig. 1).

Serious research efforts of the last decades resulted in a profound understanding of the NEMCA effect and its demonstration in many reactions and electrolyte systems [2]. It was shown that applied electrode polarisation can be used to modify the Fermi level of the catalyst surface in a controlled way [3]. By controlling the surface work function, one can control the adsorption, amount and surface diffusion properties for intermediates and partially discharged promoters. Most of the published work has been done at elevated temperature with solid oxide (YSZ) electrolyte and Pt group metal catalysts [2]. NEMCA was also proven in systems based on aqueous [4] and molten salt [5] electrolytes. Studied reactions include oxidation and reduction processes, both organic and inorganic.

The most important achievement of NEMCA's development so far is its contribution to the better understanding of the nature of a catalytical effect. The possibility for in situ tuning of a catalyst allowed for more sophisticated experiments and clarification of the role and behaviour of the oxygen backspillover species [6]. The advantage to conventional catalysis is obviously the possibility to in situ create and modify the amount of promoters on the catalyst surface by applying appropriate polarisation.

Unfortunately, NEMCA has not been commercially applied yet. The first goal of this paper is to analyse the reasons for the still missing commercial application of the NEMCA catalysis. Furthermore, potential bottlenecks for industrial applications should be identified and research directions indicated, which may open long-term opportunities for NEMCA applications.

2. Discussion

From the author's point of view there are several reasons why the NEMCA effect has not been commercially applied yet. Due to its interdisciplinary character the NEMCA catalysis has so far not found its homeland in already existing industries.

Examples for electrosynthesis applications in organic chemistry – potential entries for NEMCA market penetration – are, as is known, scarce. The main reason for that is simple, but from the author's point

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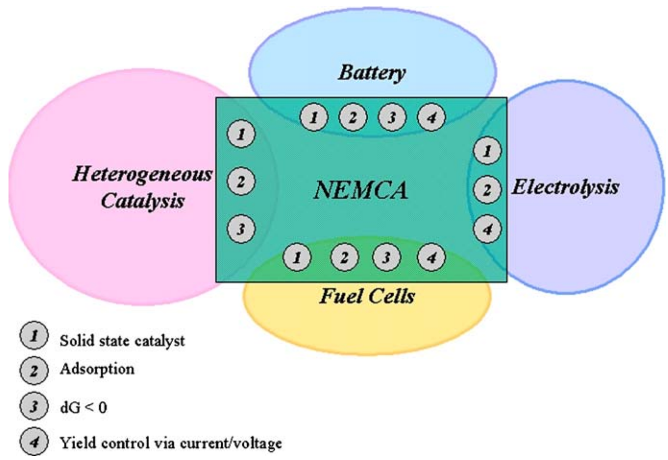

Fig. 1. NEMCA interfaces to heterogeneous catalysis, fuel cells, electrolysis and batteries.

of view probably not widely understood. The activation energy of 1 eV, common to electrochemical processes (1 V polarisation for reaction with 1e exchange) is equivalent to more than 11,000 K on the kT-scale. Obviously, such an extremely energetical activation is not the best tool for partial conversions typical for organic synthesis processes. Fuel cell technology as second potential homeland industry is just at the beginning of its commercialisation. In that stage of technology development, interest for possible spin-offs is generally limited. One could consider that as a missed, non-realized opportunity for fuel cell producers. Even a fuel cell with gas leakage between cathode and anode compartment could be a very good NEMCA reactor, where gas feeds separation is not needed. In other words, NEMCA catalysis could be a very good interim step for market introduction of fuel cell technology.

For process designers dealing with well-established chemical processes based on heterogeneous catalysis, NEMCA seems to be too radical to be easily accepted. This might change in future, when meanwhile widely spread understanding of NEMCA reaches a decision maker's level in chemical industry.

The battery relevant issues shall be discussed further in the text to follow.

To generally increase the acceptance of NEMCA and boost its commercialisation, related research has to be refocused:

(a) The mainstream focus has to be shifted from lab-scale, fundamental research, to more applied research (pilot scale tests, development of necessary manufacturing techniques etc.). Fortunately, the NEMCA development community understood that demand. An indication for that is increasing number of publications, which deal with practical aspects of NEMCA application. They address questions related to pilot plant scale tests, reactor designs but also such relevant to catalyst and electrolyte manufacturing technology. These activities were just recently excellently reviewed by Tsiplakides and Balomenou [7].
(b) To boost NEMCA commercial application it is necessary to focus appropriate research and development on right targets, right chemical processes. To identify them it is necessary to work out appropriate basic flowsheets and do first prefeasibility studies before significant effort is done on a lab-scale level. These studies might even help to work out general criteria for selection of potential NEMCA processes.
(c) The use of less expensive catalysts and electrolyte systems needs to be put in focus of further developments. If NEMCA is able to boost strongly catalytic activity why then to use expensive (Pt metal group) catalysts? Profound understanding of the electronic interactions at the catalyst surface could be the key for appropriate catalyst design developments [8]. If possible, one should use commercially available materials and semiproducts. Standardized nickel based alloys, stainless steels and/or MEAs could be used in this way as subsystems of a NEMCA reactor.

Some words related to upcoming opportunities and challenges; in the following, three topics shall be addressed:

1. Need for further fundamental studies.
2. Scale-up relevant questions to be addressed.
3. Targets for potential commercial applications.

2.1. Fundamentals

The question is if and what kind of further basic research is needed to extend the chances for commercial application of the NEMCA effect?

As already mentioned, the deep understanding of NEMCA catalysis was mainly achieved by studying noble metal catalysts combined with solid electrolytes (YSZ, yttria stabilised zirconia). Based on that, NEMCA along with clearly defined targets certainly deliver significant contributions for improvement of SOFC design. This applies for all questions related to catalysis involved (reforming, shift reaction, electrodes/electrolyte design etc.). On the other side, electrochemical promotion of catalytic activity works at lower temperatures and with other types of electrolytes as well (aqueous, molten salts and/or oxides etc.). This huge area of potential applications was scarcely studied from the NEMCA point of view in the past. Some general issues need to be also better understood, for instance those related to interactions between both, Faradaic- and non-Faradaic pathways:

- Are common intermediates needed?
- Does electrochemical promotion involve a mechanism change in the non-Faradaic reaction pathway?
- Is there a correlation between applied polarisation and activation energy change of the non-Faradaic pathway?

2.2. Scale-up

The scale-up is the next phase in NEMCA's development on its way from discovery to technology. Basically one needs larger scale reactors to verify NEMCA catalysis at larger scale throughputs (Nm^3/h, kg/h range) and in continuous mode of operation.

2.3. How to design a NEMCA reactor?

Such reactor designs are basically known from heterogeneous catalytical processes. In the case of NEMCA catalysis there is an additional challenge to master: control of electrode potential over the whole catalyst surface. There are proven technological solutions for that type of task, used to design electrolysis and fuel cells. In the case of a NEMCA reactor the task is even less difficult, since the non-Faradaic path is the productive one; yield achieved through the Faradaic path coupled to electrical current is several orders of magnitudes lower. If so, then let us use designing of NEMCA reactors the most efficient Nikola Tesla's approach for distribution of electric energy—i.e. alternative current. This may be especially applicable for NEMCA reactions with inverted volcano type of behaviour [2]. To avoid Faradaic consumption (discharge) of produced promoter one could use an asymmetric AC type of signal. There are two types of asymmetries which could be applied for that:

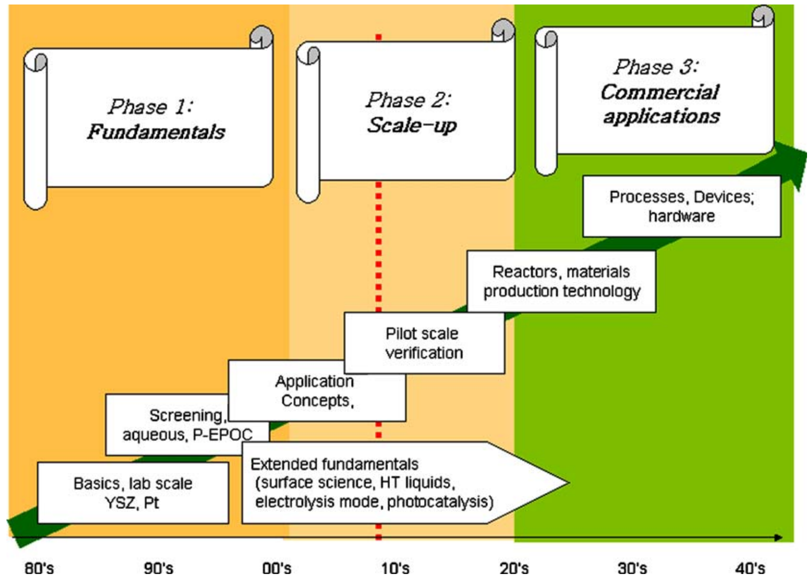

Fig. 2. NEMCA roadmap from the author's point of view.

- Promoter production half-cycle longer than discharge half-cycle (asymmetry in time).
- AC pulse superimposed on a small DC load to compensate the promoter's consumption in the discharge half-cycle (asymmetry in voltage).

To simplify reactor design one could use an induced polarisation realized in a bipolar system [9], even in combination with a single chamber reactor (SCFC) [10]. In designing such systems it is important to consider ohmic (IR) drop of the stray currents bypassing the catalyst. That IR drop must be bigger then the sum of all potential drops of the Faradaic current passing through the catalyst, to achieve catalyst operation in bipolar polarisation mode. If not, the catalyst shall experience only electrostatic interaction with surrounding electric field. By the way, a bipolar reactor despite of its simplicity cannot be considered as wireless, since both end electrodes need to be wired.

Further possibility for simplification might be a real wireless NEMCA system. Starting point for designing of an appropriate reactor would be a battery. Interestingly enough, 30 years after the discovery of NEMCA this option remained almost unexplored. Chemical energy stored in electrode(s) could be used to polarise a catalyst electrically connected to one of the electrodes. By selection of electrode composition one can set the level of electrochemical potential of the catalyst surface. This approach is not new, it is used since decades to define voltage of a battery system. Such type of NEMCA reactor could be designed to be even rechargeable. Indication for that is the behaviour of Pt electrode used for formic acid oxidation in aqueous solution. Organic oxidation continues after interruption of anodic polarisation as long as Pt-oxides created previously are available to polarise the electrode surface accordingly [11].

Similar phenomena observed during organics oxidation on IrO_2/YSZ lead few years later to the so-called permanent NEMCA [12].

To make scale-up of NEMCA reactors easier one should use proven equipment solutions and modify it accordingly. One example of that approach is the NEMCA reactor for liquid electrolytes designed on the basis of scrubber technology [13].

For commercial application of NEMCA more is needed than to design an appropriate large scale reactor. A serious engineering effort is needed to work out all process steps of an appropriate process flowsheet (conditioning of feed(s) including dedusting, reactor(s), product separation, off-gas cleaning, heat recovery etc.). Unfortunately this type of work cannot be found so far in publications dealing with NEMCA catalysis. This explains the extended predictive part of the NEMCA roadmap as presented in Fig. 2.

2.4. Applications

The question is what could be the industrially relevant targets for NEMCA.

Tree principles should be considered in the assessment of a NEMCA application for commercialisation. The first one is generic in its nature and already discussed in the previous text. Electrochemical promotion is a very powerful tool, especially suitable for activation of very slow processes. These processes if realized with conventional technologies need either extreme operating conditions (very high pressures and temperatures) or long retention times. Good candidates for NEMCA catalysis could be from this point of view for example:

- ammonia synthesis
- total oxidations at reduced O_2 partial pressure and
- direct CH_4 conversion to CxHy.

The second principle is market driven and related to the scale of the potential application. Usually, the market entrance for new technologies is easier when lower investments are required (reduced risks for first-of-its-kind applications). From this point of view the synthesis of commodity chemicals would not be the best choice for the first NEMCA application, while catalyst for car exhaust gases, on the other hand, could be a very good one. The third principle to follow is the need to use in designing of the first commercial NEMCA application as much as possible of existing established and available technologies. This would reduce appropriate implementation costs and increase acceptance for the new technological solution.

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