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The Use of Lanthanum-Based Intermetallic Compounds as a Catalyst in the Electrochemical Process of Ammonia Synthesis †

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Abstract

Functional materials based on LaCoSi and LaCuSi intermetallic compounds (IMC) were fabricated and tested in the electrocatalytic process of reducing nitrates to ammonia (NO_3RR). The method of arc melting in an argon atmosphere was used to synthesize the alloys. The synthesis process is described and analyzed in detail, and the difficulties and advantages are shown. It has been established that when using an LaCuSi-based IMC–alloy as an electrocatalyst, the reduction of nitrates is the predominant reaction. On the contrary, for the LaCoSi (IMC)–alloy electrocatalyst, NO_3RR and the hydrogen evolution reaction (HER) occur simultaneously.

Keywords: La-intermetallic compounds; synthesis of ammonia; nitrate reduction; electrocatalysis; sustainable chemistry; multicomponent catalyst

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1. Introduction

Contemporary research in hydrogen energy, as reflected in the scientific literature, encompasses a triad of key areas: the synthesis of hydrogen itself (distinguished as "brown," "blue," or "green"), the development of storage mediums like liquid organic hydrogen carriers (LOHCs) [1], and the direct application of hydrogen in synthesis. This final area involves using hydrogen in various forms—molecular, atomic, or adsorbed on a catalyst—to produce valuable chemical products.

This trend is evident in several major reviews [2,3]. For instance, review [2] highlights that electrocatalysis eliminates the need for oxidizing or reducing agents, making reactions more environmentally friendly; it also allows processes to be run at atmospheric pressure and moderate temperatures. Meanwhile, review [3] notes that in electrochemical nitrogen reduction, research focuses heavily on selecting electrode materials, as they determine the kinetic barriers for the competing reactions of reducing water to hydrogen versus nitrogen to ammonia on the electrode surface.

Intermetallic compounds (IMCs) possess ordered structures with well-defined active sites, allowing for precise control over their electronic structure and atomic ensemble size. This makes them highly promising for creating efficient catalysts, particularly for environmentally friendly electrochemical reactions like nitrogen (NRR), nitrate (NO_3RR), and

nitrite (NO_2^-RR) reduction, which are potential alternatives to the energy-intensive Haber–Bosch process. A key research goal is to develop such electrocatalysts from inexpensive, non-noble metals, partially or fully replacing noble metals [4]. To this end, using IMCs based on base metals, sometimes with minimal noble metal additives to maintain high performance, is a proposed strategy [5].

Modern environmental challenges and the need for decarbonization in the chemical industry are stimulating active research for alternative methods for the synthesis of ammonia, which is a key part of the production of fertilizers and a promising hydrogen carrier. In this case, the NO_3RR is of particular interest, which makes it possible not only to obtain a valuable product but also to solve the problem of wastewater treatment from nitrogen pollution. Recent studies demonstrate that intermetallic compounds open up new possibilities for creating highly efficient catalytic systems for this process. The aim of the work was the synthesis of La-containing IMC, and in this work, for the first time, studies were conducted on the use of La-containing IMC as catalysts in the NO_3RR reaction.

2. Materials and Methods

The synthesis of La-containing IMC by arc melting and the determination of the composition of the obtained samples by *electron probe microanalysis* and *X-ray analyzer* are described in detail in Section 3. Linear voltammetry and chronoamperometry were used to determine the optimal conditions for the reactions and synthesis of ammonia, respectively. Autolab PGSTAT302N (Metrohm AG, Herisau, Switzerland) potentiostat and PS-20 potentiostat-galvanostat with an electrochemicalimpedance (EIS) measurement module FRA (SmartStat, Chernogolovka, Russia) were used. All electrocatalytic experiments were performed in 1M NaOH with and without 10 mM $NaNO_3$ at ambient conditions. Linear voltammetry (LV) over the range between (−1.1 V) and (−1.7 V) vs. Ag/AgCl at a potential sweep rate of 50 mV s^{-1} was performed in a cathode–anode space-separated cell with a total volume of 60 mL. The auxiliary electrode was a platinum plate. The geometric area of the working electrode was 1 cm^2. The synthesis of ammonia and the NO_3RR tests were carried out for 1 h in potentiostatic mode. The determination of the ammonia content after NO_3RR was carried out with the indophenol method. UV-vis absorption spectra were recorded using a Shimadzu 3600Plus spectrophotometer (Shimadzu, Kyoto, Japan). The absorption maxima were observed at 650 nm, for which a calibration graph was plotted [5]. The most important characteristic of an electrocatalytic reaction (the Faradaic efficiency–FE %) was calculated using the formula:

$$FE(NH_3) = (8 \times F \times n(NH_3) \times 100\%)/Q \quad (1)$$

where $n(NH_3)$ denotes the amount (mol) of NH_3; F is the Faraday constant (96,485 C mol^{-1}); Q is the total charge passed through the electrode, and 8 is the number of electron transfers required to form 1 mol of ammonia.

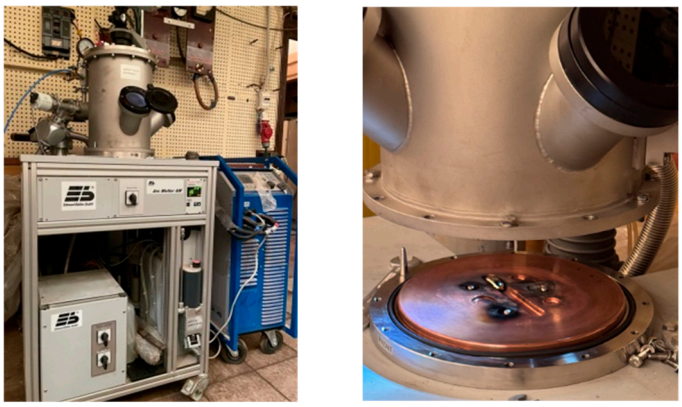
3. Results and Discussion

Starting materials for the alloy preparation were lanthanum (99.85 wt% pure), cobalt (99.95 wt%), copper (99.99 wt% pure), and monocrystalline silicon pieces (99.999%). Samples were weighed using a VIBRA HTR-220CE balance with an accuracy of 0.1 mg.

Samples of nominal composition (in atomic percents), $La_{33.3}Co_{33.3}Si_{33.3}$ and $La_{33.3}Cu_{33.3}Si_{33.3}$, were prepared by arc melting of the respective metals using a non-consumable tungsten electrode (Arc Melter AM, Edmund Bühler GmbH, Bodelshausen, Germany) on a water-cooled copper hearth under Zr-gettered argon atmosphere (Figure 1).

All buttons were remelted several times to ensure homogeneity. The overall weight losses after melting were generally less than 1 wt% of the starting weights. In order to

attain equilibrium, the samples were annealed at 800 (±5) °C for 720 h in quartz tubes that had been preliminarily evacuated and back-filled with argon, followed by quenching in cold water. The synthesis scheme is shown in Figure 2. To prepare the working electrodes for electrochemical experiments, the alloy samples were subjected to a sequence of processing steps: cutting, grinding, polishing, and final mounting in a thermosetting transparent polymer.



(**a**) (**b**)

Figure 1. (**a**) The laboratory-scale argon arc melting furnace AM with (**b**) non-consumable tungsten electrode.

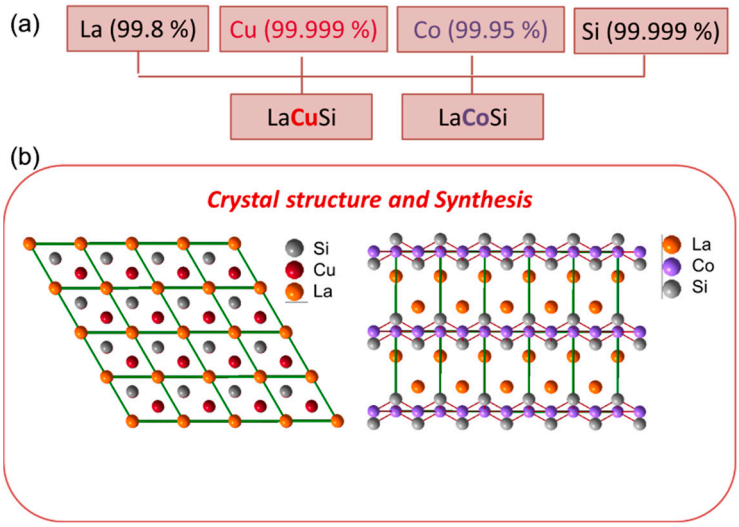


Figure 2. Schematic of the synthesis process for the LaCoSi and LaCuSi electrocatalysts: (**a**) composition of the initial charge and the synthesis outcome; (**b**) crystal structure of the intermetallic phases.

The X-ray powder diffractometer (STOE STADI-P, Darmstadt, Germany) was employed to determine the phase-structural compositions of the prepared samples. The XRD data were collected using Ge-monochromated CuKα radiation (λ = 1.54056 Å) in the 2θ range of 20–80° with a step of 0.01°. The observed diffraction intensities were compared with reference powder patterns of known ternary phases (Table 1). The alloys' compositions were controlled by electron probe microanalysis (EPMA) on the LEO EVO 50 XVP instrument (Carl Zeiss, Jena, Germany) equipped with an Oxford Instruments Inca Energy 450 energy dispersive X-ray analyzer (EDXA) (Oxford Instruments, Oxfordshire, UK).

As can be seen from Table 1, the results of the X-ray phase analysis of the $La_{33.3}Co_{33.3}Si_{33.3}$ and $La_{33.3}Cu_{33.3}Si_{33.3}$ alloys show that the lattice parameters of the corresponding intermetallic compounds are in good agreement with the literature data. It should be noted that the $La_{33.3}Cu_{33.3}Si_{33.3}$ alloy is characterized by the presence of an additional

ternary intermetallic compound, $LaCu_{0.67}Si_{1.33}$, alongside the main LaCuSi phase. Electron probe microanalysis (EPMA) confirmed the presence of two distinct phases, corresponding to dark and light regions, in the LaCuSi electrocatalyst, while revealing a single-phase composition for the LaCoSi sample (Figure 3).

Table 1. The lattice cell parameters of the annealed samples $La_{33.3}Co_{33.3}Si_{33.3}$ and $La_{33.3}Cu_{33.3}Si_{33.3}$.

IMC	a, Å	b, Å	c, Å	V, Å^3
LaCoSi	4.0724 (7)	4.0724 (7)	7.1768 (15)	119.02 (3)
LaCoSi [6]	4.069	4.068	7.17	118.90
LaCuSi	4.2680 (14)	4.0336 (10)	8.1670 (22)	128.837 (6)
LaCuSi [7]	4.268	4.268	8.167	128.8

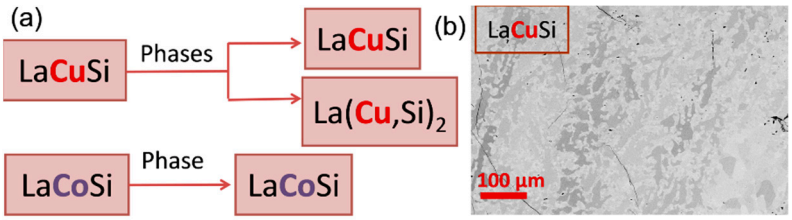


Figure 3. (**a**) Result of XRD analysis; (**b**) SEM-BSE image of a sample with the nominal composition $La_{33.3}Cu_{33.3}Si_{33.3}$.

Linear voltammetry with or without the addition of 10M $NaNO_3$ was performed to evaluate the activity of the catalyst samples in the electrochemical reaction of nitrate reduction to ammonia (NO_3RR). Next, the NO_3RR process was performed at the selected potential values. LaCoSi alloy has a low catalytic activity in the reduction of nitrates to ammonia, while LaCuSi alloy shows itself as a more active catalyst for the process, for which the maximum Faradaic efficiency reached 21.5% at a potential of −1.7 V vs. Ag/AgCl. The results and calculations are presented in Table 2.

Table 2. Faradaic efficiency for the electrocatalysts in NO_3RR (%).

Electrocatalyst	Potential of NO_3RR (Ag/AgCl)						
	−1.1 V	**−1.2 V**	**−1.3 V**	**−1.4 V**	**−1.5 V**	**−1.6 V**	**−1.7 V**
LaCoSi	1.0 ± 1.0	5.7 ± 3.0	6.5 ± 1.0	9.6 ± 1.0	7.2 ± 1.0	–	–
LaCuSi	–	2.0 ± 2.0	7.1 ± 5.0	10.1 ± 5.0	18.5 ± 2.0	18.6 ± 2.0	21.5 ± 2.5

4. Conclusions

- Functional materials based on LaCoSi and LaCuSi intermetallic compounds were obtained and tested in the electrocatalytic reaction of NH_3 synthesis;
- When using LaCuSi alloy as a cathode, the preferred reaction is the reduction of nitrates;
- When LaCoSi alloy is used as a cathode, ammonia reduction reactions from nitrates and a hydrogen release reaction occur simultaneously.

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