Micro-recycling of spent Ni-Cd batteries for the obtention of electrocatalytic coatings

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Research Article

Keywords: Spent battery valorization, circular economy, electrodeposition, cadmium-nickel alloy, hydrogen evolution reaction

Posted Date: January 14th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1189987/v1>

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Abstract

A micro-recycling approach was explored to produce catalytic metallic coatings for the hydrogen evolution reaction (HER). For this aim, discarded Ni-Cd batteries were employed as raw material. After dismantling the batteries, the active powder material, containing Cd and Ni compounds, was leached in a solution containing citric acid and hydrogen peroxide. The dissolved metals were electro-deposited on copper plates using a two electrodes cell at the following potentials (mV): -1900, -2000, and -2100 mV. The CdNi coating produced at -2000 mV, contained 92.6 % Cd and 7.4 % Ni. This coating was studied by cyclic voltammetry (CV) and potentiodynamic analysis in two different KOH solutions (0.1 M and 1.0 M). The CV analysis showed that the CdNi electrode was electrochemically stable in a wide operating voltage range (between oxygen evolution reaction and HER). Using an uncompensated resistance correction, the Tafel slopes for HER were obtained. The potentiodynamic analysis revealed that the synthesized CdNi electrode showed a catalytic activity for HER just 25.5 % smaller than the correspondent response of a standard pure Ni electrode. Our results serve as a proof of concept about the application of micro-recycling of spent batteries to produce sustainable electroactive catalytic materials for hydrogen production.

Statement Of Novelty

As a novel circular economy application, spent Ni-Cd batteries were processed under a micro-recycling approach. A cadmium-nickel alloyed metal coating was obtained as a value-added product. The catalytic activity of the coating for the hydrogen evolution reaction (HER) is around 75 % similar to pure nickel, which is considered an industrial standard for such an application. The metal coating was found to be stable in alkaline media at potentials between HER and oxygen evolution reaction (OER).

1. Introduction

Due to their high energy density and long service life, Ni-Cd rechargeable batteries have several applications, such as wireless tools and communication systems ¹. Once discarded, these devices must be safely processed ² because cadmium is an ecotoxic heavy metal ³. There exist several industrial processes for the recycling of these electric appliances, both, hydrometallurgical and pyrometallurgical ⁴. However, these industrial operations are usually located in developed countries and require large amounts of batteries, i. e. 2000–5500 MT/yr ⁵. In such a scenario, it is easy to foresee that high-scale battery recycling is not a straightforward environmental solution, suitable for most locations. In recent years, novel circular economy approaches have increased the number of options to process spent batteries. By targeting their conversion into value-added specialty products, a novel approach such as the so-called micro-recycling can be adopted ⁶. In micro-recycling, the information gathered about the characterization of the waste helps in visualizing several possible applications for the recoverable materials. Therefore, it is possible to devise cost-effective small-scale operations to facilitate the valorization of spent batteries.

Electrolytic recovery of metals for coatings manufacturing emerges as a promising micro-recycling operation to deal with battery waste. The procedure encompasses four low-tech steps, namely: mechanical dismantling, physical separation of the electroactive materials, leaching of the electroactive materials, solution treatment (filtration/conditioning), and electrodeposition of the coating ^{7,8}.

As shown in Table 1, different types of spent batteries have been used to synthesize single and multimetal coatings, either for corrosion protection or to be used as catalysts. The electrolytic obtention of catalytic materials from spent batteries has received some attention, focused on the electrooxidation of organic molecules ^{9,10}.

Given the nickel content in some battery chemistries (Ni-MH and Ni-Cd), it is possible to obtain nickel-bearing alloyed coatings by electrolytic micro-recycling. Nickel is a well-known electrocatalytic material for the hydrogen evolution reaction (HER) in alkaline media ^{11,12}. So, at least conceptually, it would be possible to obtain from spent Ni-Cd batteries alloyed coatings capable of acting as catalysts for HER.

Based on the above, this work aimed to explore the possibility of using spent Ni-Cd batteries as secondary raw material to obtain alloyed coatings under a micro-recycling approach. We evaluated the coatings to determine their electrocatalytic activity for HER in alkaline media. The assessment was conducted by comparison against a typical industrial standard, i. e., a pure nickel coating, employing electrochemical techniques. We discussed our findings in terms of a proof-of-concept for this innovative micro-recycling application. This approach can bring out implications to devise novel circular economy strategies addressing small-scale recycling procedures for spent batteries.

Table 1
Coatings for corrosion prevention and catalysts obtained from spent batteries using a microrecycling approach.

Coating type	Application	Type of battery Processed	Reference
Cobalt metal	Coating for corrosion protection in saline environment	Li-ion	13
Cobalt metal	Catalyst for glucose electrooxidation	Li-ion	9
Nickel bearing layered electrodes	Catalyst for methanol electrooxidation	Ni-Cd	10
Zn-Mn Alloy	Coating for corrosion protection in saline environment	Alkaline	14
Zn/ Zn-Ni bilayer	Coating for corrosion protection as sacrificial anode	Alkaline and Ni-MH	15
Zn/Ni-Co bilayer	Coating for corrosion protection as barrier and sacrificial anode	Alkaline and Ni-MH	16

2. Materials And Methods

2.1. Rationale

The experiments performed in this work are aimed to corroborate whether the electrodeposited metal coatings obtained from the hydrometallurgical processing of Ni-Cd spent batteries show electrocatalytic activity towards the HER in alkaline media. The effectivity of the electrodeposited electrode will be compared to pure nickel-plated electrodes, which is a well-known industrial standard catalyst for HER.

2.2. Processing of spent batteries

AA-size Ni-Cd rechargeable spent batteries were collected in the e-waste collection facilities of the Industrial University of Santander (UIS), Colombia. These devices were discharged overnight by immersion in salt water (30% NaCl). Afterward, the cells were dismantled, and the electrochemically active powder (EAP) was separated by sieving. The EAP was dried for 24 h at 100 °C and homogenized in a ball mill. The EAP was leached in a citric acid + hydrogen peroxide aqueous solution, 1250 mM and 130 mM, respectively. The solids-to-liquid ratio of the leaching procedure was 19.5 g/l. The leaching was conducted in a stirred glass reactor at 70 °C for 3 h. The leachate was recovered by filtering. This procedure granted a leaching efficiency of 75.5 wt.%. The conditioning of the solution was attained by adding concentrated HCl until pH = 1.65. This solution was used later for the electroplating process. The equilibrium speciation of Cd and Ni in the solution was estimated using free energy minimization calculations by means of the free-licensed software-package Hydra-Medusa¹⁷. For the simulation, the concentration of Ni, Cd and the ionic strength of the solution were calculated considering the reagents used in the leaching step and the typical composition of the EAP reported in the literature¹⁸. The summary of the parameters used for equilibrium calculations are shown in Table 2

Table 2
Parameters used for the equilibrium calculations using Hydra-Medusa software.

Chemical species	Initial total concentration, mM
Citrate anion (cit ³⁻)	1250.00
Hydrogen peroxide (H ₂ O ₂)	129.00
Cd ²⁺	30.75
Ni ²⁺	47.67
Cl ⁻	61.49
Ionic strength	5.81

2.3. Electroplating procedure and analysis

For the obtention of electroplated active electrodes for HER, the conditioned solution was placed in a 250 ml Pyrex® glass container, as described in Figure 1. The electrolytic cell consisted of four interconnected

nickel bars (99.0% purity) as anode and a 2 cm x 2 cm x 0.1 cm copper plate (99.9% purity) as the cathode. The copper plate was polished (2000 grit sandpaper) and sonicated in pure ethanol before being used. The cell was connected to a DC power source, and the electrodeposition was carried out for 30 min at the following constant potentials (mV): -1900, -2000, and -2100. The current response of the system was registered for each condition tested. For comparison, pure nickel electrodes were produced likewise, but at -2000 mV using a standard Watts bath ¹⁹, as a working electrolyte. The electroplated active electrodes obtained were cleansed in the ionized water and air-dried before the HER electrochemical analysis. Additionally, the surface of the electrodes was morphologically and micro-chemically analyzed by field emission scanning electron microscopy (FESEM) coupled to energy-dispersive X-ray spectroscopy (EDS) at an accelerating voltage of 25 kV in a Quanta 650 FEG (Field Emission Gun).

2.4. Electrochemical analysis of the HER on the electroplated active electrodes

The electrochemical analysis of the HER on the electroplated active electrodes was carried out using a Gamry Interface 1010B potentiostat/galvanostat. The cell consisted of a 25-ml three-electrode glass container as shown in Figure 2. The configuration of the cell was: a platinum wire as the counter-electrode, a reference Ag/AgCl (KCl sat) electrode, and the coated plate (active electrode) as the working electrode. The working electrolytes were KOH solutions of the following concentrations: 0.1 M, and 1.0 M. For each of the solutions, an open circuit potential (OCP) measurement was performed for 30 min, followed by cyclic voltammetry (CV) with a potential window from -1750 mV to +750 mV (vs. Ag/AgCl) at a sweep rate of 3 mV·s⁻¹. Afterward, the OCP measurement was repeated for 30 min, to conclude the study with a potentiodynamic analysis (PTD) between OCP value and -1750 mV vs. Ag/AgCl.

3. Results And Discussion

3.1. Electroplating process of the active electrodes for HER

After the conditioning of the leaching solution obtained from the hydrometallurgical processing of the spent batteries, the electroplating process was studied at three different voltages conditions, as shown in Figure 3.

As can be seen in Figure 3 (a) the time-dependence response of the current density (negative) varies depending upon the voltages used in the electrodeposition process. In each condition tested, namely -1900 mV, -2000 mV, and -2100 mV, the initial drop of current density took 60 s, 266 s and 300 s, respectively. These current drops are caused by the well-known depletion of metal ions at the electrodes' surface ²⁰. Thereafter, the curves at -1900 mV and -2000 mV developed a quasi-stable current, indicative of a steady-state mass transfer process during the electrodeposition ²¹. Once this plateau was surpassed, the current density increased again, in an approximated linear trend, probably due to the contribution of hydrogen evolution observed at the surface of the electrode ^{22 23}. In terms of the Faraday's law, the transferred electric charge (Q) during the process at -2000 mV was 26.4% higher ($Q_{2000} = 1.094 \text{ C.cm}^2$)

than the process at -1900 mV ($Q_{1900} = 0.866 \text{ C.cm}^2$). Very different behavior was shown by the process carried out at -2100 mV. In this case, the initial drop in current density took longer and the quasi-stable current was absent. The current increased steeply after reaching a current density minimum at 300 s. In this experiment, the transferred electric charge was $Q_{2100} = 1.953 \text{ C.cm}^2$, almost doubling the value obtained at -2000 mV. The shape of the curve can be explained, not only by the metal / hydrogen co-deposition²⁴ and bubbling-promoted convection, but also by the growth on the coating of metallic 3-D projections towards the electrolyte bulk¹⁹. Then there is an overlapping of phenomena, so that the transferred electric charge characterizes the global process.

It should be noted that all three electrodeposition voltages tested resulted in shiny metallic coatings, as shown in Figures 3 (b), (c), and (d). On the other hand, the SEM analysis of the coatings indicated some microstructural differences between the three conditions tested, as shown in Figure 4. At 1900 mV, the coating exhibited incomplete coverage (IC) on the surface, as indicated by the arrows in Figures 4 (a) and 4 (b). In contrast, the coating obtained at -2000 mV had full coverage, Figure 4 (c), with only minor defects visible at higher magnifications, Figure 4 (d). Finally, it can be seen that the coating at -2100 mV was irregular, Figure 4 (e), showing incomplete coverage as well as dendritic growth (3-D projections, TP), as indicated by the arrows in Figure 4 (f). These features are concomitant with the previously described behavior of the current density response for this condition, recorded in Figure 3 (a). Based on these microstructural characteristics, coatings electrodeposited at -2000 mV were chosen to explore electrochemical performance.

Additionally, there were some compositional differences in the coatings. In Table 3, the EDS microchemical analysis performed to the lower magnification micrographs indicated that the coatings contained cadmium and nickel. It was also observed that the content of nickel in the coatings decreased as the electrodeposition voltages increased and that the predominant metal in the coatings was cadmium.

Table 3
Normalized EDS microchemical composition of the obtained coatings shown in Figure 3.

Figure	Electrodeposition Voltage (mV)	Normalized composition (wt%)	
		Cd	Ni
Figure 3 (a)	-1900	88.5	11.5
Figure 3 (c)	-2000	92.6	7.4
Figure 3 (e)	-2100	93.8	6.2

These results could appear to be counterintuitive due to the following reasons: (i) the reduction potential of nickel is more favorable than cadmium²⁵, as follows:

and (ii) according to the speciation analysis of the solution shown in Figure 5, at pH 1.63 the leaching system, based on citric acid and hydrogen peroxide, generated a lower molar ratio for dissolved cadmium species. In this case, Figure 5 (a) shows that circa 8% of cadmium is not available for the electrodeposition because of the formation of insoluble CdCl_2 . In contrast, Figure 5 (b) indicates that only 3% of the nickel is not available for the electrodeposition, due to the formation of an insoluble nickel citrate salt, $\text{Ni}(\text{Hcit})$.

In such a scenario, nickel electrodeposition should be favored, but the results shown in Table 3 indicated that the coatings obtained were richer in cadmium. A possible explanation for this phenomenon could be given by the so-called anomalous electrodeposition²⁶, in which the less noble metal, Cd in this case, deposits preferentially than Ni in the alloyed coating. Hazotte *et al.*²⁷, reported this issue in the context of a recycling operation of Ni-Cd batteries. On the other hand, Mohanty *et al.*²⁸ showed that the presence of Cd^{2+} in the electrodeposition bath suppressed the electrodeposition of nickel, by shifting the deposition potential towards more negative values. Also, nickel electro-crystallization is a highly inhibited process²⁹, so this response of the electrodeposition system could be created by adsorbed cadmium species on the surface of the electrode. It has been reported in the literature^{30,31}, that electrodeposited Cd-Ni alloys usually form stable intermediate phases, i.e. $\beta\text{Cd}_5\text{Ni}$ and γCdNi , whose combination can be found at nickel contents between 6 % and 5 % (wt.). In this range, the normalized chemical composition of the electroplated Cd-Ni coatings is found (see Table 3).

3.2. Open circuit potential and cyclic voltammetry analysis of the electroplated active electrodes in KOH solutions.

The open-circuit potential (OCP) was measured to study the stability in KOH media of the electrodes fabricated. The cadmium/nickel electroplated active electrodes (CdNi for short), were obtained from the hydrometallurgical processing of spent batteries. Whilst the pure nickel electrodes were obtained from a typical Watts bath electroplating process. The latter was used as a standard Ni electrode for comparison. In Table 4, the obtained OCP values are reported. In both levels of KOH concentration 0.1 M and 1.0 M, the CdNi electrodes were, respectively, 214 mV and 364 mV more negative than their standard Ni counterparts. OCP values of the Ni electrode are associated with the formation of the hydroxylated nickel species on its surface³². Therefore, it is possible that the tendency to form oxidative states on the surface of the CdNi electrode is thermodynamically more favored.

Table 4
Open circuit potentials (OCP) of the electroplated electrodes in KOH media before the CV analysis.

Electroplated Electrode type	KOH Concentration (M)	OCP (mV) vs. Ag/AgCl
CdNi	0.1	- 373
Ni	0.1	- 159
CdNi	1.0	- 597
Ni	1.0	- 233

In Figure 6 and Figure 7, the CV responses for the HER and the oxygen evolution reaction (OER) are shown, respectively, for both the electroplated electrodes (CdNi and Ni) in KOH media. Figure 6 (a) shows the HER zone that is resolved for the CdNi electrode. At low KOH concentration (0.1 M) a negative current is obtained whose absolute value increases with potential. This signal is due to the hydrogen evolution reaction. Now, as the concentration of KOH in the electrolyte increases (1.0 M), the slope and magnitude of the current response with the potential acquire more negative values, which indicates an interesting behavior to produce H₂. An analogous result is obtained for the Ni electrode as it is shown in Figure 6 (b). Towards the end of the cycle, the HER on the Ni electrodes, both at 0.1 M and 1.0 M KOH, started around -1100 mV vs. Ag/AgCl. The insets in Figure 6 (a) and (b), showed the CVs throughout the entire range of explored potentials. Although these events are not easy to explain, they could be due to the formation of various species of monometallic and bimetallic hydroxides in the Cd-Ni system, as described elsewhere³⁰. In all cases, the HER results deserve to be compared from the kinetic point of view, which will be discussed in the next section.

In Figures 7 (a) and (b) the CV response towards positive potentials for the CdNi and Ni electrodes are shown, respectively. There are signs of formation of oxidized species on the surface i. e. Ni(OH)₂ and NiOOH, and towards higher potentials the current increases exponentially due to the oxygen evolution reaction. In fact, for the Ni electrode, the response obtained is comparable to that widely documented in the literature^{33 34 35 36}. In both systems (CdNi and Ni) the current intensities increase significantly when the electrolyte concentration (KOH) increases, thus indicating the catalytic benefits that oxidized nickel species provide for the redox processes that occur on both electrodes. In all cases, we compared the electrochemical performance of the CdNi electrodes obtained from spent batteries against an industrial standard for HER catalysis, namely nickel (Ni) electrodes. As previously said, these Ni electrodes were obtained by Watts-bath electroplating¹⁹. The electrochemical stability of the Ni electrodes in KOH media is shown in Figure 6 (b) and Figure 7 (b). The recorded response at 0.1 M and 1.0 M KOH reflects the typical response of nickel-metal electrodes in alkaline media^{33 34 35 36}. The CV shows in the forward scan (anodic) two events. The first one was detected at 440 mV vs. Ag/AgCl in the 1.0 M KOH experiment and at 620 mV vs. Ag/AgCl in the 0.1 M KOH experiment. This peak corresponds to the oxidation of nickel hydroxide to form NiOOH³⁷. The reverse scan (cathodic) shows a single reduction event. It occurs at 330 mV vs. Ag/AgCl in the 1.0 M KOH experiment and at 300 mV vs. Ag/AgCl in the 0.1 M KOH experiment.

These peaks are generated by the reduction of the nickel oxyhydroxide to regenerate the nickel hydroxide in the surface electrode ³⁷. In the forward scan, the second event is related to the OER which begins at 550 mV vs. Ag/AgCl in 1.0 M KOH and at 700 mV vs. Ag/AgCl in 0.1 M KOH. The increase in current is exponential as a function of potential, which is clear at the higher concentration of electrolyte.

In Table 5, the onset potential for HER on the CdNi and Ni electrodes synthesized in this work are shown. These results are compared to similar electrodes available in the literature. It can be seen that the CdNi electrodes obtained from the recycling of spent batteries have an intermediate performance between pure cadmium metal electrodes ^{38, 39} and pure nickel metal electrodes ⁴⁰. Besides, their response is rather similar to a previously described Cd/Ni(OH)₂ electrode tested for battery applications ⁴¹

Table 5
Potential conditions for HER on different electrodes containing cadmium and/or nickel.

Electrode type	Condition	Potential (mV vs. Ag/AgCl)	Scan rate mV·s ⁻¹	Reference
Cd (metal)	1 M KOH	-2055	100	38
Cd (metal)	1 M NaOH	-2055	100	38
Cd (metal)	1 M NaOH	-1905	1	38
Cd (metal)	1 M LiOH	-2105	1	38
Cd (metal)	1 M NaOH	-1735	0.1	39
Ni (metal)	0.1 M NaOH	-1026	100	40
Ni	1.0 M KOH	-1100	3	This work
Ni	0.1 M KOH	-1000	3	This work
Cd/Ni(OH) ₂	1 M KOH	-1315	10	41
CdNi	1 M KOH	-1280	3	This work
CdNi	0.1 M KOH	-1400	3	This work

3.3. Potentiodynamic analysis of HER on the electroplated active electrodes

Once completed the CV analysis for each condition, the OCP study was repeated, before performing the potentiodynamic analysis at low potential scan rate. These OCP measurements are shown in Table 6. In the case of the CdNi electrodes, the comparison of the OCP values between Table 4 and Table 6, indicates that no major changes occurred in the surface of these electrodes. The OCP variation, in this case, was

-119 and +50 mV vs. Ag/AgCl, for the 0.1 M KOH and 1.0 M KOH tests, respectively. These differences indicate that the CdNi electrode can regenerate easier immersed in KOH 1.0 M than immersed in KOH 0.1 M, possibly due to the tendency of the cadmium to react in the KOH media ³². Besides, comparing Table 4 and Table 6, the Ni electrode showed a drastic OCP change, before and after the CV analysis. Since the CVs ended at electronegative potentials, when the nickel on the electrode was in metallic form, so the second OCP registered in Table 6 shows a response compatible with a bare surface of nickel-metal ³².

Table 6
Open circuit potentials (OCP) of the electroplated electrodes in KOH media after the CV analysis and before the potentiodynamic analysis.

Electroplated Electrode type	KOH Concentration (M)	OCP (mV) vs. Ag/AgCl
CdNi	0.1	- 492
Ni	0.1	- 943
CdNi	1.0	- 547
Ni	1.0	-850

To compare the kinetic performance of the electrodes obtained to electrocatalyze the HER, a potentiodynamic analysis was carried out by evaluating only the current flow towards reduction potentials. Ni is a standard catalyst for hydrogen evolution, which is found in the second third of the volcano's curve⁴². Its activation always requires polarization, because the formation of $MH_{(ads)}$ on the surface must be promoted according to the Volmer reaction at basic pH^{43,44}, as follows:

The kinetic performance of the prepared electrodes can be seen in Figure 8(a) and Figure 9 (a), for the 0.1 M KOH experiments and in Figure 10 (a) and Figure 11 (a) for the 1.0 M KOH experiments. Therein, the current is shown as a function of potential. The apparent decay is exponential as the potential becomes more negative, highlighting the possibility that these materials must behave as convenient electrocatalysts for HER. Now, to kinetically compare the performance of the electrodes, it is convenient to estimate the Tafel slopes ⁴⁵. First, it must be evaluated if there is an uncompensated resistance (ohmic drop) that affects the measured signal, then the data must be corrected to make the Tafel plot: E vs. $\log i$ ⁴⁴. In this way, it will be possible to interpret the experimental data in relation to the microkinetic processes that characterize the HER. In fact, in the case of Ni-based materials, it is accepted that the first step involves the Volmer reaction (Eq. 3) to form MH_{ads} species, then the combination of two adjacent MH_{ads} species to form H_2 has been documented ⁴⁴ according to the Tafel reaction (Eq. 4):

The quantitative protocol for the correction of the ohmic drop, assuming current vs. potential data obtained in such a way that represents a stationary response, was carried out following the approach described in the literature ⁴⁶. Ohmic correction is reported to be important for interpreting kinetic

parameters such as Tafel slopes and others⁴⁷. The experimental current versus the potential can be written as:

$$E = a + b \ln(i) + iR \quad (5)$$

where a is the normal intercept of the traditional Tafel analysis, b is the Tafel slope and iR is the uncompensated ohmic drop. Now, deriving with respect to i we have:

$$\frac{dE}{di} = \frac{b}{i} + R$$

6

It should be noted that Eq. (6) indicates that a plot of dE/di versus $1/i$ should turn out linear with slope equal to b and an intercept equal to R . This procedure was applied to the synthesized electrodes in this work, and the results are presented in Figure 8 (b) and Figure 9 (b) for CdNi and Ni in 0.1M KOH solution, respectively and in Figure 10 (b) and Figure 11 (b) for CdNi and Ni in 1.0 M KOH solution, respectively. In all the cases, an intercept other than zero was obtained, allowing us to estimate the magnitude of the resistance considered at 0.1 M KOH, as follows: 396.03 Ohm for CdNi electrode and 70.22 Ohm for Ni electrode. At 1.0 M KOH, the magnitude of the resistance was 7.43 Ohm for the CdNi electrode and 7.26 Ohm for the Ni electrode.

Figure 8 (c) and Figure 9 (c) show the Tafel plot without correction for ohmic drop (plot E vs. $\ln i$) and it is evident that there are significant deviations from the linear behavior. On the other hand, Figure 8 (d) and Figure 9 (d) show the Tafel plot with ohmic drop correction, i. e. the $(E - iR)$ versus $\ln i$ plot. Therein, linear response with good correlation is obtained, producing Tafel slopes of 152.7 mV/Dec for CdNi and 103.0 mV/Dec for Ni, at 0.1 M KOH. Similarly, Figure 10 (c) and Figure 11 (c) show the uncorrected Tafel plot in 1.0 M KOH, for CdNi and Ni electrodes, respectively. Under this condition, both electrodes also exhibit deviation from linearity. Applying the above-mentioned correction for ohmic drop, the corrected Tafel plot $(E - iR)$ versus $\ln i$ plot is shown for the CdNi electrode in Figure 10 (d) and for the Ni electrode in Figure 11 (d). Therein, a linear response with good correlation is obtained as well, with Tafel slopes of 147.7 mV/Dec for CdNi and 151.2 mV/Dec for Ni.

Furthermore, the trend resolved in these plots reveals the presence of a unique Tafel slope for the evaluated range of current. Therefore, it is found that the H_2 evolution mechanism for a given electrode material does not depend on the magnitude of the current (or the overpotential). The values obtained for the corrected Tafel slopes are consistent with the theoretical value of the Volmer reaction, that is: 120 mV/Dec⁴³, therefore it can be precisely said that this reaction is the rate limiting step of the HER on these materials (NiCd and Ni electrodes). The differences observed in the values may be due to the interaction effects of the H_2O molecules with the electrode surface, in addition to capacitive/resistive effects caused by surface features, in each case. As explained in the literature⁴⁸, the latter can be caused by the formation of a surface oxide, but they are considered small in relation to the occurrence of the Volmer reaction.

In order to assess the HER under cathodic polarization conditions, a linear sweep voltammetry was performed for both electrodes (CdNi and Ni) at 0.1 M KOH and 1.0 M KOH. The results are shown in Figure 12. Considering the Pourbaix diagram³², thermodynamically in the experiments conducted at 0.1 M KOH, the reversible potential value for HER at the working pH is $E_{rev} = -768$ mV vs. SHE (-965 mV vs. Ag-AgCl). As can be seen in Figure 12 (a), for the CdNi and Ni electrodes the current due to HER started at potentials (E_i) equal to -1200 and -1100 mV versus Ag/AgCl, respectively. Therefore, the minimum overpotential to activate the electrodes ($E_i - E_{rev}$) for HER was estimated at: -235 mV for CdNi and -135 mV for Ni. Besides, in the experiments conducted at 1.0 M KOH, the reversible potential value for HER is $E_{rev} = -827$ mV vs. SHE (-1024 mV vs. Ag/AgCl). Thereafter, it can be noticed in Figure 12 (b), that the current due to HER started at potentials (E_i) equal to -1350 and -1175 mV versus Ag/AgCl, for both CdNi and Ni electrodes, respectively. Therefore, under this condition, the minimum overpotential to activate the electrodes ($E_i - E_{rev}$) for HER was estimated at: -310 mV for CdNi and -135 mV for Ni.

Under all the conditions tested, it must be highlighted that the minimum overpotential required to activate the electrodes was below -310 mV. On a practical level, for materials specifically designed to function adequately as catalysts for HER, the challenge is to obtain significant currents (i. e. $>10 \text{ mA}\cdot\text{cm}^{-2}$) with the condition of an overpotential of less than -500 mV⁴⁹. By inspecting Figure 12 (a), both conditions cannot be achieved when the concentration of KOH in the electrolyte is 0.1 M. Nonetheless, Figure 12 (b) shows that, at 1.0 M KOH, the potential required to achieve a current of $10 \text{ mA}\cdot\text{cm}^{-2}$ was -1557 mV for the CdNi electrode and -1327 for the Ni electrode, obtaining currents higher than those suggested for comparison ($10 \text{ mA}\cdot\text{cm}^{-2}$). Since the E_{rev} for HER at 1.0 M KOH is -1024 mV vs. Ag/AgCl, it can be readily seen that the Ni electrode shows an overpotential of -303 mV, whereas the CdNi electrode exhibits an overpotential of -533 mV.

These results indicate that the CdNi electrode synthesized through the micro-recycling approach is just 7% above the typical overpotential required in practice for HER catalysts: -533 mV for CdNi vs. -500 mV according to practical considerations. In addition, as voltage is increased Figure 12 (b) also shows that the current discharged by the CdNi electrode approaches that of the Ni electrode, indicating a rather similar behavior for both materials. In fact, at 1.0 M KOH the current registered at 1750 mV is 25.5% smaller in the CdNi electrode when compared to the Ni electrode. Specifically, the observed currents were $24.3 \text{ mA}\cdot\text{cm}^{-2}$ for the Cd-Ni electrode and $32.6 \text{ mA}\cdot\text{cm}^{-2}$ for the Ni electrode. Provided that Ni is considered a standard catalyst material for industrial generation of hydrogen from water splitting, these results are very favorable, given the facile synthesis procedure practiced in this work and that no microstructural optimization or modification whatsoever was performed to boost the electrocatalytic activity of the CdNi coating obtained from reclaimed spent batteries.

3.4. Circular economy implications of these findings

Spent batteries, particularly those containing cadmium, need proper collection, dismantling and recycling, due to the environmental hazards they comprise⁵⁰. Despite high-scale battery recycling operating in

several countries, the micro-recycling of spent batteries can also be considered. Micro-recycling is a cost-effective way to obtain value-added products from electronic waste in small-scale recycling operations ⁶. This approach is preferable in regions where logistical limitations restrain the collection and recycling of high tonnages of spent batteries ⁵.

The hydrometallurgical processing of the spent Ni-Cd batteries rendered a multimetallic aqueous solution. Using the micro-recycling approach, we successfully turned this solution into an alloyed electroplated coating. From the environmental standpoint, the electrodeposited material contains metal cadmium, a more environmentally stable form of this pollutant. It is undoubtedly advantageous because it could convey a reduction of water and soil contamination due to improper disposal of spent batteries ⁵¹. However, an application for these coatings is yet to be defined to grant a sound circular economy strategy.

At first sight, this procedure could be thought of as a downgrading of the recovered material ⁵², due to the intermixed nature of the product obtained (alloyed coating). Nonetheless, a key point for circular economy innovations implies searching for non-previously described applications for the recovered materials even if they are impure or intermixed. Due to their nickel content, we turned our research focus to determining the catalytic activity for HER of the alloyed coatings produced. Thus, in the case studied, there is an experimental confirmation that the CdNi electrode obtained through the micro recycling strategy could be useful to perform the HER and obtain the following double benefit: (i) recycling a material with potential final disposal problems and (ii) applied these materials to get an interesting and convenient product like H₂. These results are promising since they open the possibility of giving alternative applications to the materials recovered from the hydro-metallurgical recycling of discarded Ni-Cd batteries.

4. Conclusion

Our results constitute a proof-of-concept for the conversion of spent Ni-Cd batteries into alloyed coatings that can be potentially used as HER catalyst. The CdNi electrodes synthesized in this work showed catalytic activity for HER 25.5% smaller than that of pure nickel, a standard industrial reference for such a process. Moreover, the CV analysis showed that the CdNi electrode was electrochemically stable in a wide operating voltage range (between oxygen evolution reaction and hydrogen evolution reaction). However, the electrochemical response of the CdNi electrode was complex. Additionally, by calculating the uncompensated resistance that affects the measured signal in potentiodynamic tests, we were able to precisely determine the Tafel slopes for each coating synthesized, gaining insights on the microkinetic processes that characterize the HER on the CdNi and Ni substrates. Finally, the manufacturing process of the coating (hydrometallurgy/electrodeposition) needs optimization, but this aspect was out of the reach of this paper. In conclusion, this work showed that the micro-recycling of Cd-Ni spent batteries was a good approach for the obtention of an electroactive catalyst for hydrogen generation.

Declarations

Acknowledgments

The authors would like to thank Mr. Wai Liam Ng Yu for the thorough revisions and useful comments on the draft version of the manuscript. Mr. Ambrosio Carrillo and Mr. Javier Gaitan (Hydrometallurgy Laboratory, UIS) are also acknowledged for their technical support during the experimental part of this work. Finally, the authors acknowledge the Microscopy Laboratory at UIS-Guatiguará, for facilitating the SEM analysis.

Funding

The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper. The authors have no relevant financial or non-financial interests to disclose."

Author Contributions

The conception of the work, its experimental design, formal analysis, resources, funding acquisition and the drafting of the manuscript were made by Sergio Blanco and Pedro Delvasto. Héctor Rueda and Andrés Monsalve performed the data acquisition and analysis. Ronald Vargas contributed to the formal analysis of the electrochemical results and reviewed the final manuscript. All of the authors approved the version to be published.

Data Availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on request.

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Figures

Figure 1

3-D representation of the electrolytic cell used for the electroplating procedure for the obtention of catalytic coatings from spent batteries' leachate.

Figure 2

3-D representation of the three-electrode cell used for the analysis of HER.

Figure 3

Obtention of Cd-Ni coatings on copper plates using spent batteries as raw material. (a) Chronoamperometry of the electrodeposition process at 1900 mV, 2000 mV and 2100 mV. On the right, the visual appearance of the obtained coatings at (b) 2100 mV, (c) 2000 mV, and (d) 1900 mV are presented.

Figure 4

Low (left) and high (right) magnification SEM micrographs of the obtained coatings at -1900 mV (a) & (b); -2000 mV (c) & (d); and -2100 mV (e) & (f). The arrows indicate the defects observed: incomplete coverage (IC) and three-dimensional projections (TP).

Figure 5

Speciation analysis for (a) cadmium and (b) nickel, in the electrolyte solution.

Figure 6

Cyclic voltammetry analysis at negative potentials (HER zone) for the synthesized electrodes immersed in KOH media (a) CdNi electrode in 0.1 M KOH (blue) and in 1.0 M KOH (red); (b) Ni electrodes in 0.1 M KOH (orange) and 1.0 M KOH (green). In both cases, the insets show the entire potential window tested in the voltammetry analysis.

Figure 7

Cyclic voltammetry analysis at positive potentials (OER zone) for the synthesized electrodes immersed in KOH media (a) CdNi electrode in 0.1 M KOH (blue) and in 1.0 M KOH (red); (b) Ni electrodes in 0.1 M KOH (orange) and 1.0 M KOH (green).

Figure 8

HER response of the CdNi electrode at 0.1 M KOH. (a) i vs. E plot, sweep rate 3 mV·s⁻¹; (b) $\Delta E / \Delta i$ vs. $1/i$ fitting plot for uncompensated ohmic drop determination; (c) uncorrected Tafel plot, E vs. $\log |i|$; (d) corrected Tafel plot considering the calculated ohmic drop, $E - iR$ vs. $\log |i|$.

Figure 9

HER response of the Ni electrode at 0.1 M KOH. (a) i vs. E plot, sweep rate $3 \text{ mV}\cdot\text{s}^{-1}$; (b) $\Delta E / \Delta i$ vs. $1/i$ fitting plot for uncompensated ohmic drop determination; (c) uncorrected Tafel plot, E vs. $\log |i|$; (d) corrected Tafel plot considering the calculated ohmic drop, $E - iR$ vs. $\log |i|$.

Figure 10

HER response of the CdNi electrode at 1.0 M KOH. (a) i vs. E plot, sweep rate $3 \text{ mV} \cdot \text{s}^{-1}$; (b) $\Delta E / \Delta i$ vs. $1/i$ fitting plot for uncompensated ohmic drop determination; (c) uncorrected Tafel plot, E vs. $\log |i|$; (d) corrected Tafel plot considering the calculated ohmic drop, $E - iR$ vs. $\log |i|$.

Figure 11

HER response of the Ni electrode at 1.0 M KOH. (a) i vs. E plot, sweep rate $3 \text{ mV}\cdot\text{s}^{-1}$; (b) $\Delta E / \Delta i$ vs. $1/i$ fitting plot for uncompensated ohmic drop determination; (c) uncorrected Tafel plot, E vs. $\log |i|$; (d) corrected Tafel plot considering the calculated ohmic drop, $E - iR$ vs. $\log |i|$.

Figure 12

Linear sweep polarization of the Ni and CdNi electrodes in (a) 0.1 M KOH and (b) 1.0 M KOH.

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