Journal Pre-proofs

Hydrogen evolution reaction at lead/carbon porous electrodes studied by a novel electrochemical mass spectrometry set-up

Tomás M. Mondino, Gonzalo García, Elena Pastor, Fernando Fungo, Gabriel A. Planes

PII: S1388-2481(22)00195-3
DOI: https://doi.org/10.1016/j.elecom.2022.107393
Reference: ELECOM 107393

To appear in: *Electrochemistry Communications*

Received Date: 19 October 2022
Revised Date: 4 November 2022
Accepted Date: 8 November 2022

Please cite this article as: T.M. Mondino, G. García, E. Pastor, F. Fungo, G.A. Planes, Hydrogen evolution reaction at lead/carbon porous electrodes studied by a novel electrochemical mass spectrometry set-up, *Electrochemistry Communications* (2022), doi: https://doi.org/10.1016/j.elecom.2022.107393

Hydrogen evolution reaction at lead/carbon porous electrodes studied by a novel electrochemical mass spectrometry set-up

Tomás M. Mondino [a], Gonzalo García [b]*, Elena Pastor [b], Fernando Fungo[a], Gabriel A. Planes[a]**

[a]Instituto de Investigaciones en Tecnologías Energéticas y Materiales Avanzados (IITEMA-UNRC-CONICET), Departamento de Química, Universidad Nacional de Río Cuarto, Agencia Postal 3 (X5804BYA), Río Cuarto, Argentina.

[b] Instituto de Materiales y Nanotecnología, Departamento de Química, Universidad de La Laguna, PO Box 456, La Laguna, 38200, Spain.

*e-mail: ggarcia@ull.edu.es

**e-mail: gplanes@exa.unrc.edu.ar

Keywords:

Lead–acid battery; differential electrochemical mass spectrometry; Lead–carbon anode; hydrogen evolution reaction; Additive

Abstract

Lead–acid batteries are robust, low-cost, and have a large power-to-weight ratio. Recently, small amounts of carbon-based materials with a high surface area have been included in the Pb electrode as additives to improve the high-rate partial state of charge. However, carbon-based materials also enhance the hydrogen evolution reaction during the charging process at the negative active material (NAM), which is undesirable and dangerous. Therefore, in the current communication, a promising differential electrochemical mass spectrometry (DEMS) set-up suitable for studying the hydrogen evolution reaction (HER) at technical NAM electrodes in lead–acid batteries (LABs) is reported for the first time.

1- Introduction

Lead–acid batteries (LABs) were proposed by Gaston Planté in 1860 and the first report published 19 years later [1]. This was the first practical rechargeable battery and is now more than 150 years old. The formidable strength of lead–acid technology allowed it to survive for this length of time without significant changes to the central concept [2]. In this century, carbon-based materials with a high surface area have been employed to enhance the performance of lead–acid batteries [3].

The main challenge of LABs is to improve the high-rate partial-state-of-charge (HRPSoC) performance, which is important in many applications. There is strong evidence of the benefit of introducing small amounts (ca. 1–2 % w/w) of a carbon-based material with a high surface area as an additive into the lead–acid anode (Pb/C, usually called the negative active material or 'NAM') [4,5]. This inhibits sulfation and increases the capacitance and therefore the charge acceptance of the batteries [36].

However, the insertion of carbon-based materials into the NAM may also enhance the hydrogen evolution reaction (HER) during the charging process, which strongly affects the battery life cycle [3,711]. Therefore, current research is focused on the development of new materials that increase the capacitance while inhibiting sulfation and the HER at lead-based electrodes [3,12].

A number of techniques have been employed to study the HER in LABs, including volume measurements (VM), electrochemical impedance spectroscopy (EIS), rotating ring-disk electrode (RRDE), current transients (CTs) and cyclic voltammetry (CV) [1318]. It should be noted that none of these techniques provide in situ detection and quantification of the HER at lead-based electrodes. In this context, differential electrochemical mass spectrometry (DEMS) appears to be a valuable technique capable of performing in situ measurements of the onset potential of the HER as well as quantifying the amount of hydrogen produced at lead-based electrodes [1921].

In this paper we demonstrate the versatility and high sensitivity of the meniscus-based approach of a novel on-line DEMS set-up by studying the HER at technical NAM electrodes. Using this approach, H_2 is accurately detected for the first time on-line at lead-based electrodes.

2- Experimental

2.1 Electrochemical characterization

All electrochemical measurements were performed in a conventional three-electrode cell controlled by a PC Autolab potentiostat-galvanostat PGSTAT30. A reversible hydrogen electrode (RHE) was used as the reference and an activated carbon cloth as the counter electrode. All potentials in this work are given against the RHE. Experiments were carried

out in 5.0 M aqueous sulfuric solutions prepared from high purity reagents (Merck p.a.) and ultra-pure water (Millipore MilliQ gradient A10 system, 18.2 MΩ cm, 2 ppb total organic carbon). Argon (N50, Air Liquide) was used to deoxygenate all solutions.

2.2 New DEMS set-up

The electrode configuration used for the new DEMS set-up is shown in **Figure 1**. A small Pb cylinder with a central hole for a DEMS capillary tube (PTFE, Supelco®) was employed as a conductive holder. The tube is partially inserted into the Pb holder, and the end of the capillary tube sealed with a porous membrane (PTFE, Gore-Tex®) interface. The remaining space inside the Pb hole is used to hold the sample. DEMS experiments were performed using a commercial mass spectrometer from Pfeiffer (Omnistar®).

2.3 Working electrode preparation

Carbonaceous material: Two commercial carbon materials were tested: (i) HE 631 expander (Hammond®), denoted 'HE'; and (ii) SuperP Carbon black (Timcal®), denoted 'SP'.

Carbon-based ink: The suspension was prepared by stirring 20 mg of the carbonaceous material with 30 µL of Nafion® (5%, Sigma–Aldrich) and 1.0 mL of water (Milli-Q, Millipore).

DEMS measurements of technical NAM electrodes: NAM electrodes were obtained by electrochemical reduction of an aqueous mixture precursor PbO (Pb, Sigma-Aldrich), PbO + HE (Pb/HE) or PbO +SP (Pb/SP) (1 wt.% of carbonaceous material) once the NAM mixture was introduced into the Pb holder (see **Figure 1**). Then, the precursor was exposed for 1 h at ambient temperature for drying. The electrochemical reduction was carried out by applying -0.45 V vs RHE until 2.9 °C was reached. Finally, the electrode was left in Milli-Q water for

48 h, replacing the liquid every 2 h. The final size of the NAM (1 mm thick) is defined by the holder diameter and the distance from the surface to the porous membrane (ø ≈ 1.5 mm, 1 mm high). **Figure SI-1** shows representative SEM images of the NAM electrodes obtained following the procedure detailed in **Figure 1.** A porous structure with a layer thickness close to 1 mm can be observed, which is similar to that of technical (operative) LAB-NAM electrodes.

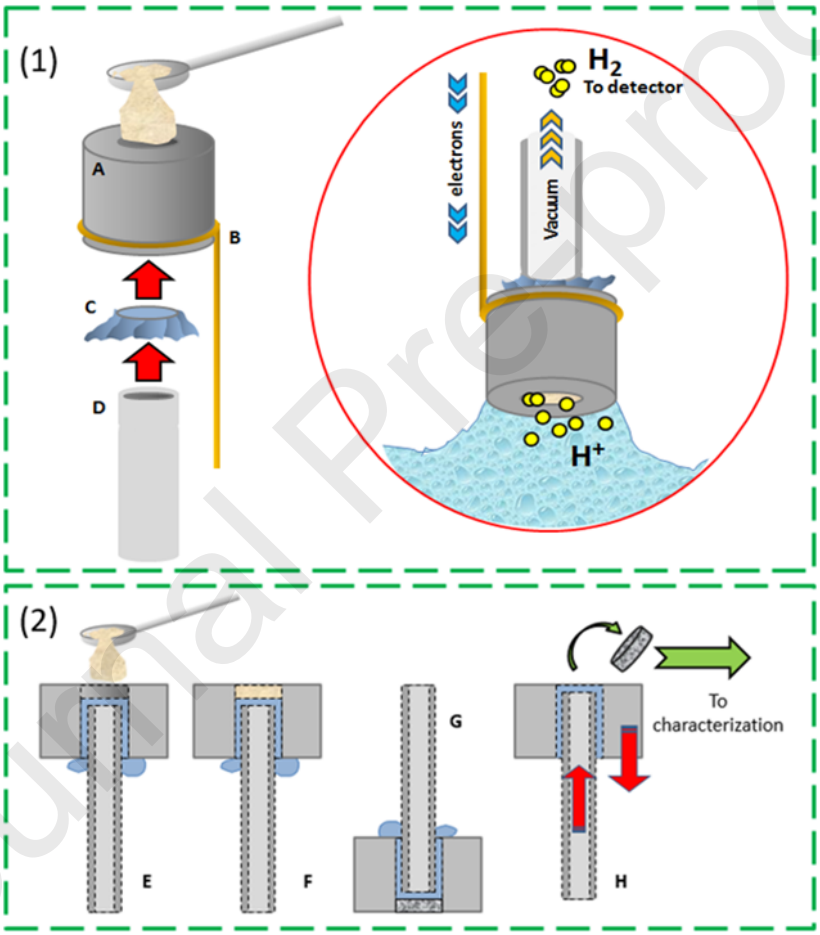


Figure 1. (1) (A) Pb holder, (B) Au wire, (C) PTFE membrane, (D) PTFE capillary; and a scheme showing the set-up in operation (right). **(2)** (E) Loading the NAM precursor (PbO or PbO/C), (F) layer formation, (G) electrochemical reduction of the precursor to give NAM (Pb or Pb/C) and subsequent electrochemical/DEMS analysis, (H) transfer of the NAM layer for further characterization.

3- Results and discussion

3.1- HER at NAM electrodes

DEMS analysis at a NAM surface is quite different from any other system examined by DEMS to date. A conventional DEMS analysis implies a thin layer porous electrode, which ensures fast tracking of any volatile species produced at any point of the electrode surface, with the behavior of current and mass signals followed on-line [20,2224].

On the other hand, a real (operative) NAM layer requires a thickness in the order of ~1 mm, which is quite a lot thicker than the typical electrodes studied by DEMS [19,22,23]. The latter size is in agreement with the electrodes synthesized in the current work (see **Figure SI-1**). Moreover, **Figure SI-2** reveals that all the electrodes tested in the current work have a specific capacity close to 100 mAh g^{-1}, which is a typical value for a conventional NAM [25]. **Figure 2** shows a cyclic voltammogram (CV) and the corresponding mass spectrometry cyclic voltammogram (MSCV) for the m/z = 2 signal recorded simultaneously at the Pb/SP electrode with a short delay of ca. 5 s, which should be ascribed to the porous structure and consequent facile diffusion of species at NAM electrodes [15,22]. It is remarkable that the ionic currents are on-line with the faradaic ones. Indeed, the MSCV for the m/z = 2 signal (H_2^+), which is associated with H_2 formation, accurately reveals the onset potential for the HER at NAM electrodes.

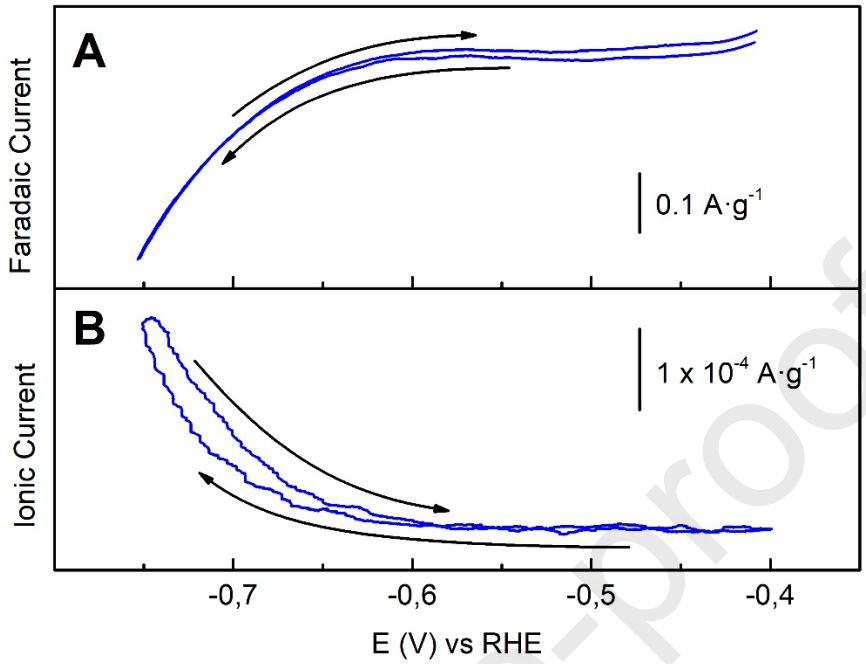


Figure 2. (A) CV and (B) MSCVs (m/z = 2) recorded at Pb/SP electrode. V = 1 mV s^{-1}; 5 M H_2SO_4. T = 25 ºC.

Figure 3 compares linear sweep voltammograms (LSVs) and the corresponding mass linear sweep voltammograms (MSLSVs) for the mass signal = 2 recorded at Pb/SP, Pb/HE and Pb electrodes. As expected, the introduction of carbon materials into the NAM enhances the HER. Indeed, the onset overpotentials for the HER increase as follows: Pb/SP < Pb/HE < Pb. On the other hand, **Figure SI-3** reveals that HE has a higher capacitance value (6.72 F g^{-1}) than SP (1.01 F g^{-1}).

Unlike the well-characterized SP carbon, HE carbon is a commercial expander provided especially for NAM applications in LABs, and contains several additives such as carbon black, lignosulfonate and barium sulfate among others, and therefore it is not possible to obtain a full physicochemical characterization of this material. Nevertheless, Figure SI-3 and

Figure 3 indicate that the HER contribution of a specific carbon surface is strongly dependent on the nature of the carbon.

It is important to recall that a high capacitance value and low HER contribution are of paramount importance in enhancing the performance of NAM electrodes, i.e. a low-cost additive with high surface area, capacitance, electrical conductivity and onset overpotential toward the HER is desirable to enhance the performance of NAM electrodes, and therefore HE appears to be a promising additive.

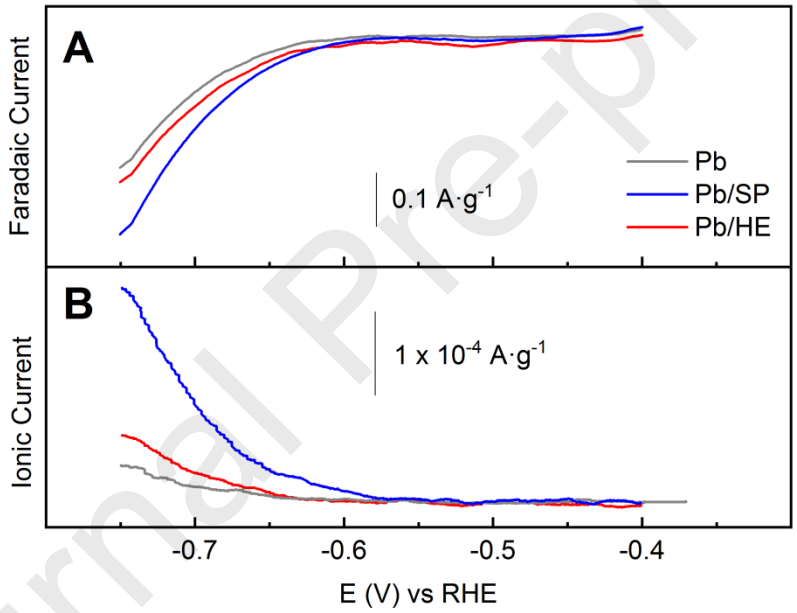
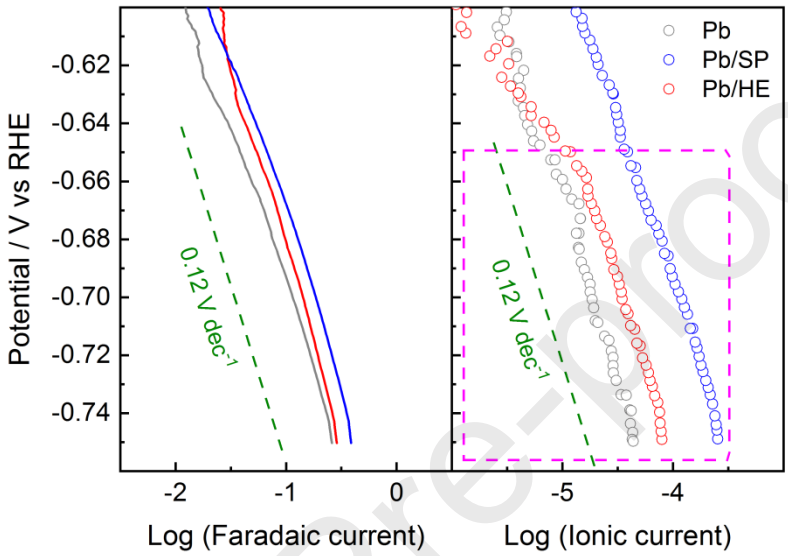


Figure 3. (A) LSVs and (B) MSLSVs (m/z = 2) recorded at Pb (grey line), Pb/SP (blue line) and Pb/HE (red line) electrodes. V = 1 mV s^{-1}; 5 M H_2SO_4. T = 25 ºC.

Finally, Tafel plots were constructed with the aim of analyzing the reaction mechanism of the HER at Pb/SP, Pb/HE and Pb electrodes. **Figure 4** shows Tafel slopes calculated from LSV and MSLSV for each sample. Interestingly, both signals (ionic and faradaic currents) reveal a Tafel slope of 0.120 V dec^{-1} which indicates that the Volmer reaction is the rate-

159 determining step (RDS), as would be expected for *sp* metals [26]. The last implies a similar
160 reaction mechanism for the HER at all materials and suggests that the exchange current
161 density (i_0) is the main parameter affected by the nature of the additive.

162



163

164 **Figure 4**. Tafel plots achieved with faradaic (left panel) and ionic (m/z = 2, right panel) for Pb (grey),
165 Pb/SP (blue) and Pb/HE (red) electrodes. The green lines have a slope of 120 mV dec^{-1}. V = 1 mV s^{-1};
166 5 M H_2SO_4. T = 25 ºC.

167

168 **4- Conclusion**

169 A novel electrochemical mass spectrometry was developed and applied to follow the
170 hydrogen evolution reaction (HER) in situ at technical negative active materials (NAMs)
171 employed in lead–acid batteries (LABs). Using this approach, accurate onset potentials and
172 reaction mechanisms for the HER at NAM electrodes were determined for the first time. The
173 novel DEMS set-up appears to be a valuable technique for studying the HER at NAM
174 electrodes in operando during the charging process of LABs.

175

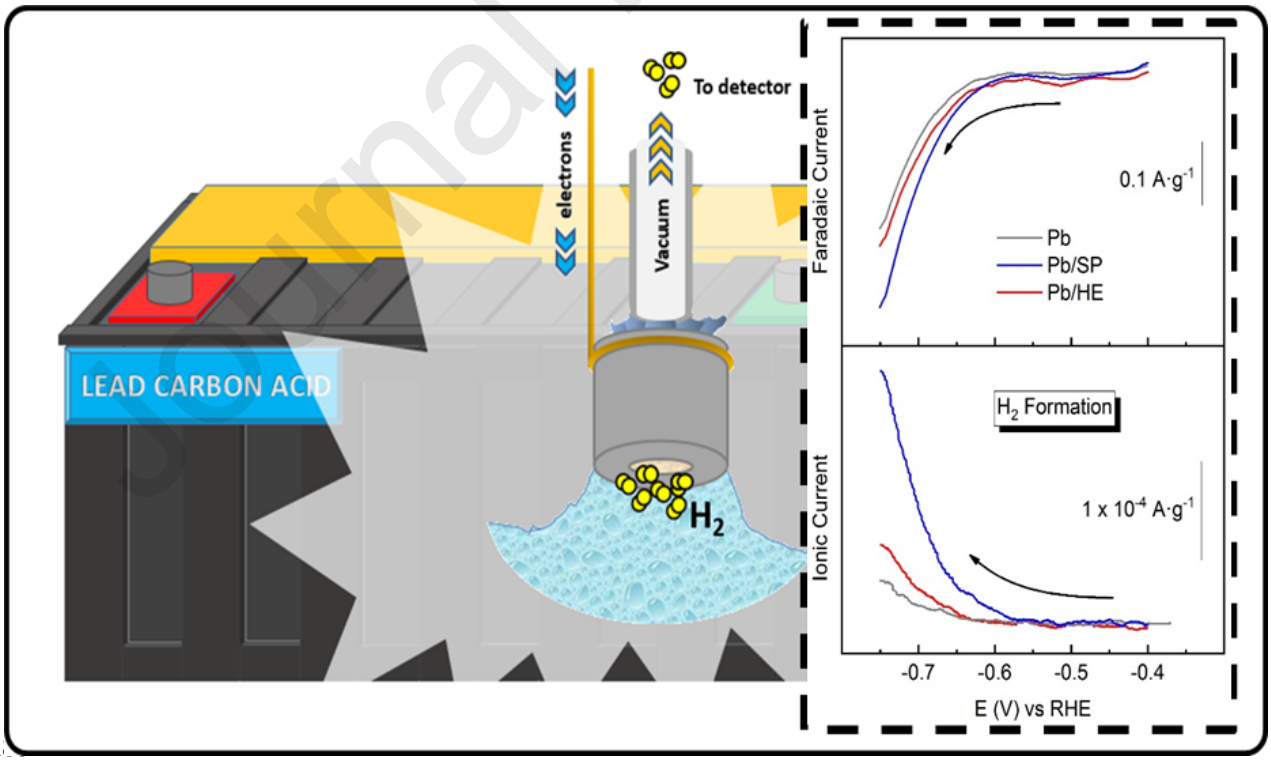
ACKNOWLEDGMENTS

The authors acknowledge financial support of this work by grants from MINCyT-Córdoba (PIODO 2018) and Secretaría de Ciencia y Tecnica (SECyT), UNRC (PPI) Argentina. F.F, and G.A.P. are permanent research staff of CONICET. T.M.M. thanks Pla-Ka S.A. and CONICET for doctoral scholarships. In addition, this work has been supported by the Ministerio de Ciencia e Innovación (MCIN) under projects PCI2020-112249 and PID2020-117586RB-I00 funded by MCIN/AEI/10.13039/501100011033, and by the Canarian Agency for Research, Innovation and Information Society (ACIISI, ProID2021010098). G.G. acknowledges NANOtec, INTech, Cabildo de Tenerife and ULL for laboratory facilities.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data to this article can be found online at ***.

REFERENCES



Highlights

- DEMS is employed to study a lead/carbon anode for use in a lead–acid battery (LAB)
- A new DEMS setup makes it possible to follow the HER at the Pb/carbon anode.
- Independent measurement of HER expands the study of reaction mechanisms in LABs

CRediT author statement

Conceptualization, G.G., G.A.P., E.P. and F.F.; methodology, T.M.M.; validation, G.G., G.A.P., E.P. and F.F.; formal analysis, G.G. and G.A.P.; data curation, T.M.M.; writing—original draft preparation, G.G. and G.A.P.; writing—review and editing, G.G. and G.A.P.; funding acquisition, G.G., G.A.P., E.P. and F.F. All authors have read and agreed to the published version of the manuscript.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

219

[1] S.P. Thompson, Recherches sur l'Électricité, Nature 21 (1879) 150.

[2] P. Kurzweil, Gaston Planté and his invention of the lead–acid battery—The genesis of the first practical rechargeable battery, J. Power Sources 195 (2010) 4424-4434. https://doi.org/10.1016/j.jpowsour.2009.12.126

[3] P.T. Moseley, D.A.J. Rand, A. Davidson, B. Monahov, Understanding the functions of carbon in the negative active-mass of the lead–acid battery: A review of progress, J. Energy Storage 19 (2018) 272-290. https://doi.org/10.1016/j.est.2018.08.003

[4] R. Marom, B. Ziv, A. Banerjee, B. Cahana, S. Luski, D. Aurbach, Enhanced performance of starter lighting ignition type lead-acid batteries with carbon nanotubes as an additive to the active mass, J. Power Sources 296 (2015) 78-85. https ://doi.org/10.1016/j.jpowsour.2015.07.007

[5] H. Yang, Y. Qiu, X. Guo, Lead oxide/carbon black composites prepared with a new pyrolysis-pickling method and their effects on the high-rate partial-state-of-charge performance of lead-acid batteries, Electrochim. Acta 235 (2017) 409-421. https://doi.org/10.1016/j.electacta.2017.03.138

[6] H.Y. Hu, N. Xie, C. Wang, F. Wu, M. Pan, H.F. Li, P. Wu, X.D. Wang, Z. Zeng, S. Deng, M.H. Wu, K. Vinodgopal, G.P. Dai, Enhancing the performance of motive power lead-acid batteries by high surface area carbon black additives, Appl. Sci. 9 (2019) 186. https://doi.org/10.3390/app9010186

[7] J. Xiang, C. Hu, L. Chen, D. Zhang, P. Ding, D. Chen, H. Liu, J. Chen, X. Wu, X. Lai, Enhanced performance of Zn(II)-doped lead-acid batteries with electrochemical active carbon in negative mass, J. Power Sources 328 (2016) 8-14. http://dx.doi.org/10.1016/j.jpowsour.2016.07.113

[8] D. Pavlov, P. Nikolov, T. Rogachev, Influence of carbons on the structure of the negative active material of lead-acid batteries and on battery performance, J. Power Sources 196 (2011) 5155-5167. https://doi.org/10.1016/j.jpowsour.2011.02.014

[9] M. Blecua, E. Fatas, P. Ocon, J. Valenciano, F. de la Fuente, F. Trinidad, Influences of carbon materials and lignosulfonates in the negative active material of lead-acid batteries for microhybrid vehicles, J. Energy Storage 11 (2017) 55-63. https://doi.org/10.1016/j.est.2017.01.005

[10] L.T. Lam, R. Louey, Development of ultra-battery for hybrid-electric vehicle applications, J. Power Sources 158 (2006) 1140-1148. https://doi.org/10.1016/j.jpowsour.2006.03.022

[11] L. Wang, W. Zhang, L. Gu, Y. Gong, G. Cao, H. Zhao, Y. Yang, H. Zhang. Tracking the morphology evolution of nano-lead electrodeposits on the internal surface of porous carbon and its influence on lead-carbon batteries, Electrochim. Acta 222 (2016) 376-384. https://doi.org/10.1016/j.electacta.2016.10.189

[12] P.T. Moseley, D.A.J. Rand, K. Peters, Enhancing the performance of lead–acid batteries with carbon – In pursuit of an understanding, J. Power Sources 295 (2015) 268-274 https://doi.org/10.1016/j.jpowsour.2015.07.009

[13] M.A. Deyab, Effect of halides ions on H_2 production during aluminum corrosion in formic acid and using some inorganic inhibitors to control hydrogen evolution, J. Power Sources 242 (2013) 86-90. https://doi.org/10.1016/j.jpowsour.2013.05.066

[14] Y.M. Wu, W.S. Li, X.M. Long, F.H. Wu, H.Y. Chen, J.H. Yan, C.R. Zhang, Effect of bismuth on hydrogen evolution reaction on lead in sulfuric acid solution, J. Power Sources 144 (2005) 338-345. https://doi.org/10.1016/j.jpowsour.2004.10.019

[15] K. Jo, E. Hwang, A quantitative evaluation of oxygen reduction and hydrogen evolution reaction contributions to Pb corrosion, J. Electroanal. Chem. 850 (2019) 113393. https://doi.org/10.1016/j.jelechem.2019.113393

[16] S. Kang, M. Shang, M.A. Spence, M. Andrew, S. Liu, J. Niua, Dynamic charge acceptance and hydrogen evolution of a new MXene additive in advanced lead-acid batteries via a rapid screening three-electrode method, Chem. Commun. 54 (2018) 3456-3459. https://doi.org/10.1039/C8CC00086G

[17] S. Zhang, H. Zhang, W. Xue, J. Cheng, W. Zhang, G. Cao, H. Zhao, Y. Yang, A layered-carbon/$PbSO_4$ composite as a new additive for negative active material of lead-acid batteries, Electrochim. Acta 290 (2018) 46-54. https://doi.org/10.1016/j.electacta.2018.08.090

[18] F. Wang, C. Hu, M. Zhou, K. Wang, J. Lian, J. Yan, S. Cheng, K. Jiang, Research progresses of cathodic hydrogen evolution in advanced lead–acid batteries, Sci. Bull. 61 (2016) 451-458. https://doi.org/10.1007/s11434-016-1023-0

[19] S. Pérez-Rodríguez, G. García, M.J. Lázaro, E. Pastor, DEMS strategy for the determination of the difference in surface acidity of carbon materials, Electrochem. Commun. 90 (2018) 87-90. https://doi.org/10.1016/j.elecom.2018.04.014

[20] S. Díaz-Coello, G. García, M.C. Arévalo, E. Pastor, Precise determination of Tafel slopes by DEMS. Hydrogen evolution on tungsten-based catalysts in alkaline solution, Int. J. Hydrogen Energy 44 (2019) 12576-12582. https://doi.org/10.1016/j.ijhydene.2019.02.151

[21] G. García, M. Roca-Ayats, O. Guillén-Villafuerte, J.L. Rodríguez, M.C. Arévalo, E. Pastor, Electrochemical performance of α-Mo2C as catalyst for the hydrogen evolution reaction, J. Electroanal. Chem. 793 (2017) 235-241. https://doi.org/10.1016/j.jelechem.2017.01.038

[22] R. Ianniello, V.M. Schmidt, A simplified DEMS set up for electrocatalytic studies of porous PtRu alloys, Ber. Bunsenges. Phys. Chem. 99 (1995) 83-86. https://doi.org/10.1002/bbpc.19950990114

[23] C. Niether, M.S. Rau, C. Cremers, D.J. Jones, K. Pinkwart, J. Tübke, Development of a novel experimental DEMS set-up for electrocatalyst characterization under working conditions of high temperature polymer electrolyte fuel cells, J. Electroanal. Chem. 747 (2015) 97-103. https://doi.org/10.1016/j.jelechem.2015.04.002

[24] M. Heinen, Y.X. Chen, Z. Jusys, R.J. Behm, In situ ATR-FTIRS coupled with on-line DEMS under controlled mass transport conditions—A novel tool for electrocatalytic reaction studies, Electrochim. Acta 52 (2007) 5634-5643. https://doi.org/10.1016/j.electacta.2007.01.055

[25] D. Pavlov, Lead-Acid Batteries: Science and Technology. A Handbook of Lead-Acid Battery Technology and Its Influence on the Product, second ed., Elsevier, 2017. ISBN 978-0-444-59552-2.

[26] G. Zhao, W. Sun, Electrochemical hydrogen evolution reaction. In: J. Ma (Ed.), Photo- and Electro-Catalytic Processes, Wiley, 2022, Chapter 3. https://doi.org/10.1002/9783527830084.ch3