Table 2
Magnetic characteristics of PAni + FeO (1:0.6) composite.

Composite	M_S, emu/g	M_0, emu/g	H_c, Oe
1	11.5	1.26	177
2	15.3	1.26	160

current efficiency is also the highest for these three entries.

For PAni + FeO (1: 1) - 2 composites before and after the electrohydrogenation process, the specific surface area values were determined (BET method, Sorbi MS instrument), and found to be 31.3 m^2/g and 23.7 m^2/g, respectively. It is obvious that the forming PAni + Fe^0 + FeO + Fe_3O_4 cathodic coating with a large specific surface affects the hydrogen overvoltage potential, which decreases in alkaline catholyte solution [20,21], and electrohydrogenation of *p*-NBA as a whole.

In spite of the fact that, in this work, the electrohydrogenation products were not isolated and identified, it can be assumed, referring to the studies carried out in [18,19], that the electrohydrogenation of *p*-NBA in an alkaline medium on the novel PAni + Fe^0 + FeO + Fe_3O_4 cathodic coating with a large specific surface area includes both mechanisms (EP and ECH), and the main product is *p*-aminobenzoic acid.

The powders of the initial PAni + FeO + Fe_3O_4 composites deposited on a horizontally located cathode are maintained on its surface by an out-cell magnet. In the course of the studies, it was observed that composites after electrohydrogenation of *p*-NBA have better magnetic properties than the initial composites. Table 2 reports the magnetic properties of the composite PAni + FeO (1:0.6) before (*1*) and after (*2*) electrohydrogenation of *p*-NBA: M_S is the saturation magnetization, M_0 the residual magnetization, and H_c the coercive force. This composite was chosen because of its good performance as an electrocatalyst (see Table 1, entry 5).

According to the data in Table 2, composite *2* is characterized by a higher saturation magnetization and lower coercive force than composite *1*. Evidently this is facilitated by the appearance of crystalline phases of metallic iron in the constitution of composite *2*. The obtained iron- and iron-oxides-containing PAni composites with these magnetic characteristics can be classed as soft magnetic materials having many applications in a variety of fields.

4. Conclusions

PAni + FeO + Fe_3O_4 composites were prepared by the introduction of iron (II) oxide into the reaction medium of oxidative polymerization of aniline. The composites deposited as a powder on a Cu cathode were electroactive in the electrochemical reduction of *p*-nitrobenzoic acid in aqueous NaOH. The electrocatalytic activity was evidenced by the hydrogenolysis of the intermediate *p*-hydroxylaminobenzoate to the aminobenzoate and is attributed to the formation of iron in the zero-valence state as a result of the electrochemical reduction of Fe^{2+} cations of FeO. In addition, the magnetic properties of PAni + FeO (1:0.6) composite before and after the electrohydrogenation process were studied and suggest that the iron- and iron oxides-containing PAni composites obtained can be classed as soft magnetic materials.

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References

[1] A.D. Pomogailo, A.S. Rosenberg, I.E. Uflyand, Metal Nanoparticles in Polymers, Khimiya, Moscow, 2000.
[2] L. Nicolais, G. Carotenuto, Metal-Polymer Nanocomposites, John Wiley & Sons Inc., Hoboken, New Jersey, 2005.
[3] I.Yu. Sapurina, Ya. Steyskal, The effect of pH on the oxidative polymerization of aniline and the morphology and properties of products, Russ. Chem. Rev. 79 (2010) 1123–1143, https://doi.org/10.1070/RC2010v079n12ABEH004147.
[4] Z. Wang, H. Bi, J. Liu, T. Sun, X. Wu, Magnetic and microwave absorbing properties of polyaniline/γ-Fe_2O_3 nanocomposite, J. Magn. Magn. Mater. 320 (2008) 2132–2139, https://doi.org/10.1016/j.jmmm.2008.02.043.
[5] W. Shen, M. Shi, M. Wang, H. Chen, A simple synthesis of Fe_3O_4 nanoclusters and their electromagnetic nanocomposites with polyaniline, Mater. Chem. Phys. 122 (2010) 588–594, https://doi.org/10.1016/j.matchemphys.2010.03.051.
[6] S.S. Umare, B.H. Shambharkar, R.S. Ningthoujam, Synthesis and characterization of polyaniline-Fe_3O_4 nanocomposite: electrical conductivity, magnetic, electro-chemical studies, Synth. Met. 160 (2010) 1818–1821, https://doi.org/10.1016/j.synthmet.2010.06.015.
[7] A.C.V. de Araujo, R.J. de Oliveira, S. Alves Junior, A. Rodrigues, F.L.A. Machado, F.A.O. Cabral, W.M. de Azevedo, Synthesis, characterization and magnetic properties of polyaniline-magnetite nanocomposites, Synth. Met. 160 (2010) 685–690, https://doi.org/10.1016/j.synthmet.2010.01.002.
[8] S. Khasim, S.C. Raghavendra, M. Revanasiddappa, K.C. Sajjan, M. Lakshmi, M. Faisal, Synthesis, characterization and magnetic properties of polyaniline/γ-Fe_2O_3 composites, Bull. Mater. Sci. 34 (2011) 1557–1561, https://doi.org/10.1007/s12034-011-0358-x.
[9] K. Basavaiah, Y. Pavan Kumar, A.V. Prasada Rao, A facile one-pot synthesis of polyaniline/magnetite nanocomposites by micelles-assisted method, Appl. Nanosci. 3 (2013) 405–415, https://doi.org/10.1007/s13204-012-0148-y.
[10] T. Bashir, A. Shakoor, E. Ahmad, M. Saeed, N.A. Niaz, S.K. Tirmizi, Structural, morphological and electrical properties of polyaniline-Fe_2O_3 nanocomposites, Polym. Sci. Ser. B 57 (2015) 257–263, https://doi.org/10.1134/S1560090415030021.
[11] B. Kim, S. Chae, H.J. Choi, Fabrication of polyaniline coated iron oxide hybrid particles and their dual stimuli-response under electric and magnetic fields, Express Polym Lett 9 (2015) 736–743, https://doi.org/10.3144/expresspolymlett.2015.68.
[12] V.V. Tolmacheva, V.V. Apyari, E.V. Kochuk, S.G. Dmitrienko, Magnetic adsorbents based on iron oxide nanoparticles for the extraction and preconcentration of organic compounds, J. Anal. Chem. 71 (2016) 321–338, https://doi.org/10.1134/S1061934816040079.
[13] S.P. Gubin, Yu.A. Koksharov, G.B. Khomutov, G.Yu. Yurkov, Magnetic nanoparticles: preparation, structure and properties, Russ. Chem. Rev. 74 (2005) 489–520, https://doi.org/10.1070/RC2005v074n06ABEH000897.
[14] N.M. Ivanova, E.A. Soboleva, Ya.A. Visurkhanova, I.V. Kirilyus, Electrocatalytic activity of polyaniline-copper composites in electrohydrogenation of *p*-nitroaniline, Russ. J. Electrochem. 51 (2015) 166–173, https://doi.org/10.1134/S1023193515020056.
[15] N.M. Ivanova, E.A. Soboleva, Ya.A. Visurkhanova, Bimetallic Co-Cu polyaniline composites: structure and electrocatalytic activity, Russ. J. Appl. Chem. 89 (7) (2016) 1072–1081, https://doi.org/10.1134/S1070427216070053.
[16] L. Shi, Y.D. He, X.H. Xia, Z.M. Jian, H.B. Liu, High rate capability of Fe/FeO/Fe_3O_4 composite as anode material for lithium-ion batteries, J. Iran. Chem. Soc. 7 (2010) 721–726, https://doi.org/10.1007/BF03246062.
[17] J. Stejskal, R.G. Gilbert, Polyaniline. Preparation of a conducting polymer, Pure Appl. Chem. 74 (2002) 857–867, https://doi.org/10.1351/pac200274050857.
[18] E.S. Chan-Shing, D. Boucher, J. Lezzard, The electrochemical reduction of α-nitrocumene in a protic and basic medium on large surface area (poros) electrodes: electronation-protonation or electrocatalytic hydrogenation? Can. J. Chem. 77 (1999) 687–694, https://doi.org/10.1139/v99-035.
[19] J. Lessard, Electrocatalytic hydrogenation, in: O. Hammerich, B. Speiser (Eds.), Organic Electrochemistry, 5th ed., CRC Press, Boca Raton, FL, 2016, pp. 1657–1672.
[20] H. Wendt, V. Plzak, Electrocatalytic and thermal activation of anodic oxygen- and cathodic hydrogen-evolution in alkaline water electrolysis, Electrochim. Acta 28 (1983) 27–34, https://doi.org/10.1016/0013-4686(83)85083-X.
[21] O. Savadogo, F. Carrier, The hydrogen evolution reaction in basic medium on iron electrodeposited with heteropolyacids, J. Appl. Electrochem. 22 (1992) 437–442, https://doi.org/10.1007/BF01077546.