PAPER • OPEN ACCESS

Effect of graphite addition into mill scale waste as a potential bipolar plates material of proton exchange membrane fuel cells

To cite this article: D S Khaerudini et al 2018 J. Phys.: Conf. Ser. 985 012050

View the article online for updates and enhancements.

You may also like

- <u>Challenges in Scientific Data</u> <u>Communication from Low-mass Interstellar</u> <u>Probes</u> David G. Messerschmitt, Philip Lubin and Ian Morrison
- Bulk Aging of Graphite-Polypropylene Current Collectors Induced by Electrochemical Cycling in the Positive Electrolyte of Vanadium Redox Flow Batteries Barbara Satola, Lidiya Komsiyska and Gunther Wittstock
- <u>Electrochemical Aging and</u> <u>Characterization of Graphite-Polymer</u> <u>Based Composite Bipolar Plates for</u> <u>Vanadium Redox Flow Batteries</u> Gaurav Gupta, Barbara Satola, Lidiya Komsiyska et al.





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 18.119.131.72 on 02/05/2024 at 21:45

Effect of graphite addition into mill scale waste as a potential bipolar plates material of proton exchange membrane fuel cells

D S Khaerudini, G B Prakoso, D R Insiyanda, H Widodo, F Destyorini and N Indayaningsih

Fuel Cell Group, Research Center for Physics, Indonesian Institute of Sciences, Gd. 440 Kawasan Puspiptek Serpong, Tangerang Selatan 15314, Banten, Indonesia

E-mail: deni008@lipi.go.id

Abstract. Bipolar plates (BPP) is a vital component of proton exchange membrane fuel cells (PEMFC), which supplies fuel and oxidant to reactive sites, remove reaction products, collects produced current and provide mechanical support for the cells in the stack. This work concerns the utilization of mill scale, a by-product of iron and steel formed during the hot rolling of steel, as a potential material for use as BPP in PEMFC. On the other hand, mill scale is considered a very rich in iron source having characteristic required such as for current collector in BPP and would significantly contribute to lower the overall cost of PEMFC based fuel cell systems. In this study, the iron reach source of mill scale powder, after sieving of 150 mesh, was mechanically alloyed with the carbon source containing 5, 10, and 15 wt.% graphite using a shaker mill for 3 h. The mixed powders were then pressed at 300 MPa and sintered at 900 °C for 1 h under inert gas atmosphere. The structural changes of powder particles during mechanical alloying and after sintering were studied by X-ray diffractometry, optical microscopy, scanning electron microscopy, and microhardness measurement. The details of the presence of iron, carbon, and iron carbide (Fe-C) as the products of reactions as well as sufficient mechanical strength of the sintered materials were presented in this report.

1. Introduction

In recent years, due to the demand of energy consumption continuously increasing along with the depletion of resources, the development and research on renewable energy is essential to overcome this energy issue. Proton exchange membrane fuel cells, as one of the most promising renewable energy technology for stationary, portable and automotive applications, have attracted much attention mainly because of their light weight, low operating temperature and producing electricity from electrochemical reactions in an environmentally friendly manner [1]. PEMFC consists of various components, among which bipolar plates allocate about 60 to 80% of PEMFC weight and 30 to 45% of their cost [2], hence one of the most important components of PEMFC due to their volume and cost.

The bipolar plates are typically made from graphite, composite, and metal plates [3]. With respect to corrosion resistance, graphite is preferable. However, the conductivity of this material is still much lower than that of metallic one. The machining cost of graphite BPP is very high, which account for as much as 60% of the stack cost. The porous nature and brittleness of graphite also prevent people from utilizing it. Extensive works have been made to develop alternative BPP materials to replace it [4].

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd 1

Alternatives fall into composite and metallic based BPP. It has been estimated that for composites and metal plates, the cost of BPP would be only 15 to 29% of the stack cost [5]. Due to their high strength, metallic BPP can be made of very thin sheets with a thickness of 0.1 mm or less [6-9]. Therefore, metallic BPP is considered as the most important substitute for graphitic ones, due to ability to mass production and decreasing PEMFC volume and weight, which lower the overall manufacturing cost [10]. Low cost materials are also essential for fruitful combination of PEMFC into the commercial energy sector [11]. As an alternative one, waste-based materials can also be utilized as raw materials, for instance mill scale. Mill scale is a waste material from the steelmaking industry and considered has rich iron content (about 70 - 75% Fe). Thus, the high content of Fe in mill scale is potentially used as raw material for manufacturing metallic-based BPP. In this study, in order to reduce the cost as well as to utilize the industrial mill scale waste, we report a study of the utilization of mill scale based BPP with some variation addition of graphite for evaluation and justification on their microstructural, physical, and mechanical properties.

2. Experimental

In the present study, the industrial mill scale (as received from PT Krakatau Steel, Cilegon, Indonesia) the chemical composition (wt.%) of Fe total: 74.24%, Fe metal: 0.20%, Fe₂O₃: 52.02%, SiO: 0.25%. CaO: 0.97%, MgO: balance (analyzed by XPS), was chosen as raw material. After sieving of 150 mesh and preparing the substrate sample, the graphitic material as a carbon source was added with variation of 5, 10, and 15 wt.%. The carbon was considered to lead the formation of Fe-C, specifically in their austenite phase. Thus, the blends was mechanically alloyed using a shaker mill in a discontinues milling manner with milling speed of 600 rpm, delay time of 20 minutes, and total milling time of 3 h. To prepare the green body, the milled powders were pressed with 300 MPa load at room temperature into the mould with diameter of 20 mm and targeted thickness of 3 mm. The green body was then sintered at 900 °C for 1 h under inert gas atmosphere. After grinding and polishing, the samples obtained were microstructure analyzed by optical microscopy (OM Bestscope BS6000AT) and scanning electron microscopy (SEM Hitachi SU 3500). Phase analysis was carried out by X-ray diffraction (XRD SmartLab, Rigaku) with a copper anode x-ray tube with 20 from 10 to 90° using a 0.01° step size and 0.25 second count time. To measure the surface hardness of sample, Vickers hardness was analyzed by Microhardness Tester (HV Leco LM100AT).

3. Results and discussion

3.1. Phase characterization

The X-ray diffraction analysis was used to identify the phase present in the material during the sintering process. Figure 1 shows the XRD peaks profile for sample in the powder (before sintering) and solid (after sintering) state. From the as received mill scale, it was known that iron oxides were the predominant substances in the material before mixing and the amount of metallic iron is not significant (0.20%). For the powder of pure mile scale (0 wt.% addition) as shown in figure 1a, the presence of wustite (FeO) and magnetite (Fe_3O_4) was recorded. At this condition the ferritic (Fe) phase was not detected, indicating insignificant of metallic iron or due to very low intensity of Fe peak. However, for the sintered sample it shows very high peaks of Fe species at 20 value of 44.354° with reflection index of (001). For all mixing powder with various addition of graphite after milling for 3 h (figure 1b, 1c, 1d), it has shown typical peaks profile that detected only wustite and magnetite, the difference is only wider peaks compared with the pure one (figure 1e). The wider peaks of mixing powder can be contributed due to the finer size of graphite powder; however the peak of graphite itself still cannot detected this due to the origin of requirement of much higher sinter temperature (>> 2000 °C) of graphite compared with the ferritic based material (mill scale). In this study, one can be considered the graphite also act like a "binder" or "matrix" for the mixing product of mill scalegraphite. This benefit for its homogenous bonding of Fe-C; yet it is still far from their ideal sinter condition. For the sintered mill scale-graphite (solid), one can see that the Fe species also could be detected, even though not the highest peak one, at 2 θ about 70 to 80°. This showed that the flowing of inert gas and sintering process at 900 °C are suitable to converts the metal oxide (FeO or Fe₃O₄) that are present in mill scale into pure Fe, although still in the α -Fe (ferritic) phase; whereas, the desired phase in this study is the austenite (γ -Fe) phase.



Figure 1. XRD patterns of milled powder and solid sample with graphite addition of (a) 0, (b) 5, (c) 10, (d) 15 wt.%, and (e) XRD patterns of original mill scale, graphite, and 5 wt.% of powder samples. The obtained phases are wustite (FeO), magnetite (Fe₃O₄) and ferritic (Fe).

The presence of ferritic is due to the origin of mill scale that starting emerged the iron species after sintering at 900 °C and flowing under inert atmosphere. From the evidence of XRD, there are two possibilities occurred. (i) The 'thermal energy' of sintering temperature causing the oxygen element in the metal oxide 'diffuse-out' of the matrix in a mill scale and allow the formation of new species, such as iron (Fe). Other one, (ii) it can be due to the nature of impurities that probably contained in the chemical composition of mill scale that will affect into their sintering temperature and process. Therefore, the presence of impurities makes graphite difficult to diffuse-out and react with the mill scale (Fe species) compound; for instance become Fe₃C, so that no atomic bonding reactions or alloy phase occurred between the elements on the mill scale-graphite at the condition of 900 °C.

3.2. Vickers hardness

3rd International Symposium on Frontier of Applied Physics (ISFAP 2017)	IOP Publishing
IOP Conf. Series: Journal of Physics: Conf. Series 985 (2018) 012050	doi:10.1088/1742-6596/985/1/012050

Vickers hardness test was carried out on the surface of the sintered sample to evaluate Fe-C bonding with respect of graphite addition. The optical micrographs of the penetrated area after diamond indentation showed wider diamond flaking zone (not shown here) with increasing of graphite addition. Microhardness values of the samples are shown in figure 2. As clearly seen, the pure mill scale sample (0 wt.% graphite addition) have the highest microhardness (320.8 VHN) than the graphite added samples. The lowest microhardness value is 103.53 VHN belong to sample with 15 wt.% graphite addition. Thus, the sample shows a decrease in hardness with increasing of graphite addition. This is probably due to low interfacial bonding of Fe-C caused by inappropriate sintering temperature at 900 °C condition. One should consider that the desired sintering temperature of pure graphite must be higher than 2000 °C. Therefore, the initial stage for diffusion process of Fe-C shows incomplete bonding. However, when it was compared with the commercial pure graphite of BPP, i.e. 24 HVN (directly measured in our lab), the obtained hardness values are still much higher. One can be rationalised from the above results are due to the origin of low hardness value of graphite itself, when mixed with the mill scale (ferritic based materials) it will contribute into lower hardness value. This also inferred that the desired Fe-C phase (Fe-C bonding) at sinter condition of 900 °C is not fully achieved. Therefore, the samples are probably still in the composite state.



Figure 2. Vickers hardness result of the sample with graphite addition of 0 to 15 wt.%.

3.3. Micrograph analysis

Figure 3 shows SEM top view images of all sintered samples with respect of graphite addition of 0, 5, 10, and 15 wt.% after sintering at 900 °C for 1 h. It clearly shows a significant morphology different between with and without graphite addition. The pure mill scale based sample (figure 3a) shows inhomogeneous grain structure morphology while the graphite added samples (figures 3b, 3c, 3d) show relatively homogenous. At this condition, all samples still show some pore morphology. However, with increasing of graphite addition the pore morphology shows decrease. For the pure mill scale (0 wt.% graphite addition), the main reason of such pore morphology can be addressed due to the various of its original elemental/compound composition of mill scale that not totally react at sinter condition of 900 °C. Hence, the imperfect phase transformation process and diffusion between each compound causing such inhomogeneous morphology. This also probably can be explained due to different of diffusion rates and some different of lattice movement between each compound of mill scale so that causing such different of grain size and shape as well as its pore morphology existence.

doi:10.1088/1742-6596/985/1/012050



Figure 3. SEM micrograph of the sintered sample with graphite addition of (a) 0, (b) 5, (c) 10, and (d) 15 wt.%.

In the pure mill scale sample, indeed the pore structures are still exist; However, in term of hardness level, the pure one is the highest one. This can be explained due to its better compound bonding (as clearly showed in figure 4a) where the grain boundary is formed at this condition, even not fully yet homogenous. While the 15 wt.% graphite addition sample (figure 4b), the grain boundary is difficult to be identified. Therefore, this grain boundary state most probably contribute into its better hardness value of pure mill scale (0 wt.% graphite addition) than the graphite added samples. Figure 5 shows the optical micrograph of all samples. One can be seen that with increasing graphite addition the density of the 'white colour' is increasing. It means the graphite is distributing more with increase its addition number.



Figure 4. Comparison of SEM micrograph images of the sintered sample with (a) 0 and (b) 15 wt.% graphite addition at magnification of 5000x and 15000x.

IOP Conf. Series: Journal of Physics: Conf. Series **985** (2018) 012050 doi:10.1088/1742-6596/985/1/012050



Figure 5. Optical micrograph images of the sintered sample with graphite addition of (a) 0, (b) 5, (c) 10, and (d) 15 wt.%.

4. Conclusions and future work

In this report, the elaboration of using mill scale-based bipolar plate material for PEMFC was studied. We fabricated with variation of graphite addition (0, 5, 10, 15 wt.%) and sintered at 900 °C for 1 h under inert gas atmosphere. The XRD analysis revealed that the obtained phases are wustite (FeO) and magnetite (Fe₃O₄), while for the sintered sample the ferritic (Fe) phase is also can be detected, inclusive for the pure mill scale. The hardness evaluation showed that the pure sample is much higher (320.8 VHN) than the graphite added samples. This is tentatively distributed to the not optimum sinter condition of mill scale-graphite. The micrograph analysis showed the grain boundary morphology of the pure mill scale sample. While the added graphite samples are hardly to be identified, however, their graphite distribution can be confirmed by its optical micrograph results. Those results suggest that the mill scale waste has some potential application as bipolar plate material; however it still need further research investigation and evaluation prior to their ideal bipolar plate component application.

Acknowledgments

The authors would like to thank Dr Bambang Prihandoko for raw material support, the Research Center for Physics – LIPI for technical and facilities support.

References

- [1] Wee J H 2007 Renew. Sustain. Energy Rev. 11 1720
- [2] Feng K, Li Z, Sun H, Yu L, Cai X, Wu Y and Chu P K 2013 J. Power Sources 222 351
- [3] Karimi S, Fraser N, Roberts B and Foulkes F R 2012 Adv. Mater. Sci. Eng. 2012 828070
- [4] Oyarce A 2013 Electrode degradation in proton exchange membrane fuel cells (Doctoral Dissertation) (Stockholm: KTH Royal Institute of Technology) p 77
- [5] Taherian R 2014 J. Power Sources **265** 370
- [6] Rajasekar S, Chetty R and Neelakantan L 2015 Int. J. Hydrog. Energy 40 12413
- [7] Zhou T Y and Chen Y S 2015 J. Fuel Cell Sci. Technol. 12 051001
- [8] Jung S P, Lee C I, Chen C C, Chang W S and Yang C C 2015 J. Power Sources 283 429
- [9] Tawfik H, Hung Y and Mahajan D 2007 J. Power Sources 163 755
- [10] Lu C D, Mao P Z, Wen D H and Jia H 2013 Key Engineering Materials 546 164
- [11] Shimpalee S, Lilavivat V, McCrabb H, Khunatorn Y, Lee H K, Lee W K and Weidner J W 2016 *Int. J. Hydrog. Energy* **41** 13688