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GENERATION OF HIGH PURITY HYDROGEN FROM STEEL INDUSTRY WASTE

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ABSTRACT
An economically viable and environmental friendly method of generating hydrogen feed for fuel cells is by the reaction of certain metals with steam, appropriately called ‘metal-steam reforming’ – MSR. An inexpensive source of iron for the MSR is the mill-scale waste from steel industry. Mill-scales have been traditionally reduced to pure iron via hydrogen and carbothermic reduction processes both of which are quite energy-intensive. In our research, however, the use of high temperature and hydrogen has been eliminated by a novel solution-based technique whereby nanoscale iron powder is produced at room temperature. This paper discusses some preliminary results of an investigation carried out to convert steel industry waste into nanoscale iron which was subsequently used in generating hydrogen.

INTRODUCTION
Hydrogen, an ideal energy-carrying medium for fuel cells, particularly the PEMFCs is not as abundant a commodity in nature as oxygen and nitrogen and must be derived from other natural resources such as fossil fuels or water. In the light of the serious economic constraints and safety concerns associated with production, storage and supply of gaseous hydrogen, one needs to find ways and means of its generation, storage, transportation and supply to the end use port - in more reversible, much simpler and far safer ways.

An economically viable and environmental friendly method of generating hydrogen is by the reaction of certain metals with steam, also appropriately called ‘steam-metal reforming’. For example, the reaction which occurs around 600ºC has long been known as one of the promising ways of generating H₂ (Otsuka et al., 2001, 2002, 2003; Takenaka et al., 2004; Santoss and Maurao, 2004):

$$3 \text{Fe} + 4 \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4 \text{H}_2 \quad (1)$$

The reverse reaction could be viewed as a hydrogen storage scheme. The theoretical amount of hydrogen being stored is 4.8 wt% which corresponds to ca. 4211 L H₂/L Fe at STP. A perceived design for generating hydrogen via metal-steam reforming consists of the following. Iron is packed into cartridges and loaded on the vehicles. Addition of water to the pre-heated cartridges produces pure humidified hydrogen that could be supplied directly to PEMFC on the vehicles. The cartridges with corresponding oxides after water decomposition could be exchanged with the new ones. The oxide is again reduced to ready-to-use active metal later. Thus, the process of H₂ generation via MSR in an efficient and cyclic fashion consists of: (a) iron-steam reaction and, (b) reduction of the spent iron oxide into active elemental iron for the next cycle.

However, the task of making this process technologically viable and sustainable is challenging. Most importantly, the kinetic of metal oxidation (forward) and oxide reduction (reverse) as per reaction (1) ought to be significantly improved, in order to mitigate sintering and coarsening of iron and iron oxide particles during repeated generation-conversion cycles. With this goal, we have developed an effective technique of producing H₂ by using the so-called ‘mill-scale’ waste from steel industry, as an iron source, in a way that is consistent with the most sought-after criteria: environment, availability and price. The mill-scale is a hard brittle coating of several distinct layers of iron oxides formed during the processing of steel. It is predominantly Fe₃O₄ and magnetic in nature with iron content ranging between 66 to 88% depending upon the source and conditions employed for its stripping from the steel.

We have recently carried out a systematic and thorough investigation on steel waste material to establish the feasibility of hydrogen production and recycling of the oxide on a laboratory scale. It was found that the mill-scale samples could be quantitatively (~100%) reduced to elemental iron, both via H₂ and carbothermic reduction, as has been demonstrated by others. However, with an objective to eliminate the use of high temperature and H₂ gas and, to mitigate the CO and/or CO₂ emission, a solution-based technique has been devised resulting in the formation of nanoscale elemental iron particles from mill-scale powder at room temperature. The metal-steam reforming experiments carried out using the nano iron...
powder derived from mill-scale magnetite waste showed that conversion of water into hydrogen as per reaction (1) was near stoichiometric (≥ 95%).

EXPERIMENTAL
Sample processing
Mill-scale samples were procured from three different vendors: North American Steel (KY), Midrex (NC) and Nucor-Yamato (AR). The samples from North American Steel were labeled as pickled (NAS-P), sludge rinse (NAS-S) and entry loop (NAS-E) by the supplier, referring to the chemical treatments used for stripping the oxide layer from the steel structures. Samples from Midrex and Nucor-Yamato are hereafter referred to as MR and NY, respectively, for brevity. All the five mill-scale samples were ball-milled followed by attrition-milling in 2-propanol and sieved through 325 mesh (average particle size ≤ 45 μm) prior to any processing or characterization. Hydrogen reduction of the sieved mill-scale powders was carried out at 900°C for 8h using high purity dry H2 at ~101 kPa. For the carbothermic reduction, the sieved mill-scale powders were mixed with activated carbon in the molar ratio of 1:3, pelletized with small amount of polyvinyl alcohol to aid compaction and heated at 1100°C for 4h, using nitrogen as a blanket gas. The carbothermic reaction can be represented as:

Fe₃O₄ + 3C → 3Fe + 2CO + CO₂ (2)

As mentioned earlier, regeneration of elemental iron from the spent oxide via hydrogen or carbothermic reduction is an energy-intensive process and hence undesirable in a commercial setting. To obviate these commercial predicaments the milled and sieved samples were digested in mineral acid and treated with aqueous sodium borohydride solution in the presence of sodium hydroxide as pH stabilizer (pH ~6.8) (Forster et al., 1999). This resulted in immediate precipitation of nanoscale iron particles – a clear advantage over the agglomeration seen during hydrogen and carbothermic reduction. The iron powder was thoroughly washed with DI water and acetone.

Metal-steam reforming reaction
Metal-steam reforming experiments were carried out in a stainless steel tubular reactor at 600°C. A thermocouple placed in the proximity of the specimen monitored the temperature. Helium was used as an inert background during the temperature ramp. After the sample attained the desired temperature, a 50:50 v/v mixture of steam (water preheated to 400°C) and He was introduced into the reactor at ambient pressure. The reaction was allowed to run until no hydrogen signal was detected in the mass spectrometer attached to the reactor at the outlet.

Characterization
Chemical analysis of the as-received mill scale samples was done by X-ray fluorescence (XRF) technique. The X-ray powder diffraction patterns on the raw, reduced and post-MSR samples were collected at room temperature on a Philips diffractometer (PW 3050/60 X’pert Pro), using monochromatic CuKα₁ radiations (λ = 1.54056 Å) and Ni filter. Morphology of the samples before and after reduction and steam reforming were examined by a Philips scanning electron microscope (XL30 FEG). The morphology and crystal structure of the nanoscale iron particles were studied by transmission electron microscopy (JEOL 3010) operated at 300 kV equipped with selected area electron diffraction (SAED) and the energy dispersive spectroscopy (EDS). Hydrogen yield in the MSR reaction was quantified by a quadrupole mass spectrometer (QMS 200, Pfeiffer Vacuum Omnistar).

RESULTS AND DISCUSSION
Table I shows the XRF analyses of the as-received mill-scale samples from various vendors. As can be seen, two of the three NAS samples were predominantly rich in Cr (52 to 67% by weight), while the third sample contained about 18% Cr and 8% Ni by weight. On the other hand, MR and NY samples contained 92-94 wt% Fe and no significant Cr or Ni. The presence of chromium in significant amounts has serious implications on the environmental aspects of the process. Hence, if the NAS samples were to be used for the H₂ production, one has to isolate Fe which means disposing nickel and hexavalent chromium, the latter being a known health hazard in water system. Since Ni and Cr-ferrites are difficult to breakdown, preliminary reduction experiments failed to generate elemental iron quantitatively from NAS samples, as revealed by XRD patterns and corroborated by thermogravimetric experiments. Hence, they were not used further.
Table I. XRF analyses of the mill scale samples used in this study.

<table>
<thead>
<tr>
<th>M</th>
<th>NAS-P</th>
<th>NAS-S</th>
<th>NAS-E</th>
<th>Midrex</th>
<th>Nucor-Yamato</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>29.13</td>
<td>42.3</td>
<td>70.42</td>
<td>93.92</td>
<td>92.91</td>
</tr>
<tr>
<td>Cr</td>
<td>66.57</td>
<td>51.59</td>
<td>18.11</td>
<td>0.16</td>
<td>0.168</td>
</tr>
<tr>
<td>Mn</td>
<td>2.75</td>
<td>2.49</td>
<td>1.4</td>
<td>1.19</td>
<td>1.3</td>
</tr>
<tr>
<td>Ni</td>
<td>0.178</td>
<td>0.872</td>
<td>8.24</td>
<td>0.232</td>
<td>0.189</td>
</tr>
<tr>
<td>Ca</td>
<td>-</td>
<td>0.128</td>
<td>-</td>
<td>1.33</td>
<td>3.14</td>
</tr>
<tr>
<td>Si</td>
<td>0.332</td>
<td>0.267</td>
<td>0.357</td>
<td>1.49</td>
<td>1.05</td>
</tr>
<tr>
<td>Mo</td>
<td>0.282</td>
<td>1.3</td>
<td>0.53</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>0.337</td>
<td>0.366</td>
<td>0.608</td>
<td>0.515</td>
</tr>
<tr>
<td>V</td>
<td>0.412</td>
<td>0.259</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

On the other hand, hydrogen and carbothermic reduction of MR and NY samples resulted in complete conversion of the scales NY, which confirm the above statement. Gravimetric analyses of the samples before and after reduction gave an average weight loss of 27.5 wt% (hydrogen reduction) and 27 wt% (carbothermic reduction) for the MR and NY samples, respectively; this agrees very well with the theoretical value of 27.64 wt% for the Fe$_3$O$_4$ to Fe reduction.

The morphology of the mill-scales before and after hydrogen reduction is compared in Fig. 2, while the microstructural features of the MR and NY samples after carbothermic reduction are shown in Fig. 3. Figure 4a and 4b shows the morphology of the iron particles derived by using sodium borohydride aqueous solution from the Midrex and Nucor-Yamato samples, respectively.

Fig. 1. XRD patterns of the as-received and reduced MR and NY samples.
Fig. 2. SEM features of the mill-scale samples: (a) MR, and (b) NY. 1- before and 2- after H$_2$ reduction.

Fig. 3. Morphology of the carbothermically reduced samples: (left) MR, (right) NY.

Fig. 4. SEM micrographs of solution-derived iron nanoparticles from Midrex and Nucor-Yamato waste.
The TEM images, the EDS spectrum and XRD pattern of the nanoscale iron particles derived from acidic solution of Midrex samples are shown in Fig. 5, 6 and 7, respectively; Cu and Mo traces in the EDS originate from the Cu-Mo grid used for the TEM imaging. The broad diffraction peak belonging to the most strong <110> reflection of elemental iron (fcc) further demonstrates the formation of nanoscale iron; the crystallite size calculated from the Scherrer equation (Cullity, 1978), is ~26 nm. The SAED pattern of the nanoscale iron is showed in Figure 8. The diffraction rings belong to the (110), (200) and (211) planes of bcc iron.

Fig. 5. TEM images of iron particles obtained by room temperature processing. Scale bar: 20 nm.

Energy dispersive X-Ray

![Energy dispersive X-Ray spectrum](image)

Fig. 6. TEM-EDS pattern of the solution-derived nano iron.
Fig. 7. X-ray diffractogram of the solution-derived nanoscale iron.

Fig. 8. Selective area electron diffraction pattern of the solution-derived nanoscale iron.
Figure 9 compares the results of metal-steam reforming (MSR) carried out with carbothermically and H\textsubscript{2} reduced NY sample and the nano-iron obtained via aqueous reduction. It can be seen that for a 90% conversion value, higher activity with regard to H\textsubscript{2} generation is dominant if nano-Fe is used as compared to that derived from the other two techniques. It is interesting, however, to note that irrespective of the source from which iron for MSR was acquired, the magnetite formed after the steam reformation can be dissolved in mineral acids from which highly active nano-iron is again recovered. Figure 10 shows the scanning electron micrographs of the NY sample before and after metal-steam reforming reaction using nanoscale iron.

Fig. 9. Time dependence of the hydrogen generation during MSR from Nucor-Yamato samples.
Fig. 10. Morphological artifacts of the NY samples before (top) and after (bottom) MSR using nanoscale iron obtained from aqueous borohydride reduction of the mill-scale.
CONCLUSIONS
Metal-steam reforming using iron is a safe and economically viable method of hydrogen generation from inexpensive raw materials for ready PEMFC utilization. An attractive and inexpensive source of iron is the waste from the steel industry in the form of magnetite, provided it can be reduced to metallic iron. In this work we have shown that, two of the five mill-scale samples from commercial vendors were quantitatively reduced to iron via hydrogen reduction, and carbothermic processes at high temperatures. A novel solution-based technique using sodium borohydride as the reductant yielded nanoscale iron with an average particle size of ~40 nm. Optimization of the latter process also obviated the formation of sodium borate as a by-product and hence the need for its separation. The hydrogen production via metal-steam reforming reaction represented by reaction (1) shows that the nanoscale iron possesses a higher propensity of reaction with steam than that derived via either of the high temperature reduction processes adopted here, under identical experimental conditions. Furthermore, the spent oxide can be quantitatively recycled to yield highly active nanoscale metallic iron again by an acid dissolution route without the loss of its reactivity, thereby maintaining the hydrogen generation capacity of the starting material over several cycles. Work is in progress for the search of an alternative inexpensive yet equally potent reductant in lieu of sodium borohydride.

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REFERENCES


