Review on Hydroelectric Cell with Nanomaterial for Generation of Green Energy

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ABSTRACT

As increasing demand of electricity, there should be some alternative sources for generating electricity. Hydroelectric Cell (HEC) is an innovative alternative for producing green energy source by spitting of water. HEC has anode of Zinc plate and cathode of silver with Lithuim-substituted magnesium ferrite as electrolyte. When HEC is partially dipped in water, spontaneously hydroxide and hydronium ions are produced by water molecule dissociation. Hydronium ions trapped in nanopores develop enough electric field that further dissociates water molecules. This works shows the detail review of mechanism and thermodynamics of Hydroelectric Cell (HEC) working.

Keywords*: Grotthus Chain Reaction, Nano Material, Sintering, Sputtering*

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1. INTRODUCTION

Increasing demand in various sector like power, steel, and cement, the demand and supply gap for various resources led to a rise in the import of resources. Current energy planning in India is dependent on conventional source like coal, oil, natural gas and other fossil fuel. But today the scenario is that there is a shortage of conventional sources. So to fulfill the need, we have to dependent on other countries, which is badly effect our economic and social development as shown in fig-1 [1]. Also when there is a shortage of crude oil, we have to pay high rate to purchase it. India stand fourth rank in the world total energy combustion and it is increasing with development sector to meet demand. So it is necessary to find an alternative path to fulfill a current requirement and future demand. The crisis of electricity in rural areas in comparison to urban areas seems to be biased in delivery through the centralized system. While the urban-rural difference in energy supply can be reduced through renewable energy. But it is more difficult to convert and storage of electricity and hence it requires direct supply to grid system to overcome the gap. Pressure to increase its energy supplies and the consequent negative environmental impact of fossil fuels has led India to a conscious policy toward renewable sources is very effective. But today we face one of major problem with renewable energy system is storage and conversion of it. Because many renewable source are depend on nature, which produces an excess electricity of some of the time and not enough at other. So critical situation says that storage of excess production otherwise it is going to a waste. There have been a lot of efforts to make use of water/water vapour as electrical energy source, but a little success has been achieved in this direction. Recently, graphene oxide-based battery of a 0.1 cm2 area at 70% relative humidity has been demonstrated to produce a maximum of 2 μW power in presence of electrolyte [2]. Picowatt power generation using jumping water droplet from super hydrophobic surface to hydrophilic surface is also reported [3]. Cement matrix, along with water, has also been explored as a battery using different combination of electrodes [4]. A very low current of 0.1mA has been obtained out of a 7×7×4cm3 cement electrolyte mould [5].

Hydroelectric Cell (HEC) is an innovative alternative for producing green energy source by spitting of water. HEC has anode of Zinc plate and cathode of silver with Lithuim-substituted magnesium ferrite as electrolyte. When HEC is partially dipped in water, spontaneously hydroxide and hydronium ions are produced by water molecule dissociation. Hydronium ions trapped in nanopores develop enough electric field that further dissociates water molecules. This works shows manufacturing and experimental analysis of Hydroelectric Cell. In the present

scenario, all electrochemical cells having dissimilar electrodes, for example, dry cell, Zinc-silver oxide battery and other cells essentially electrolyte to generate electrical current.
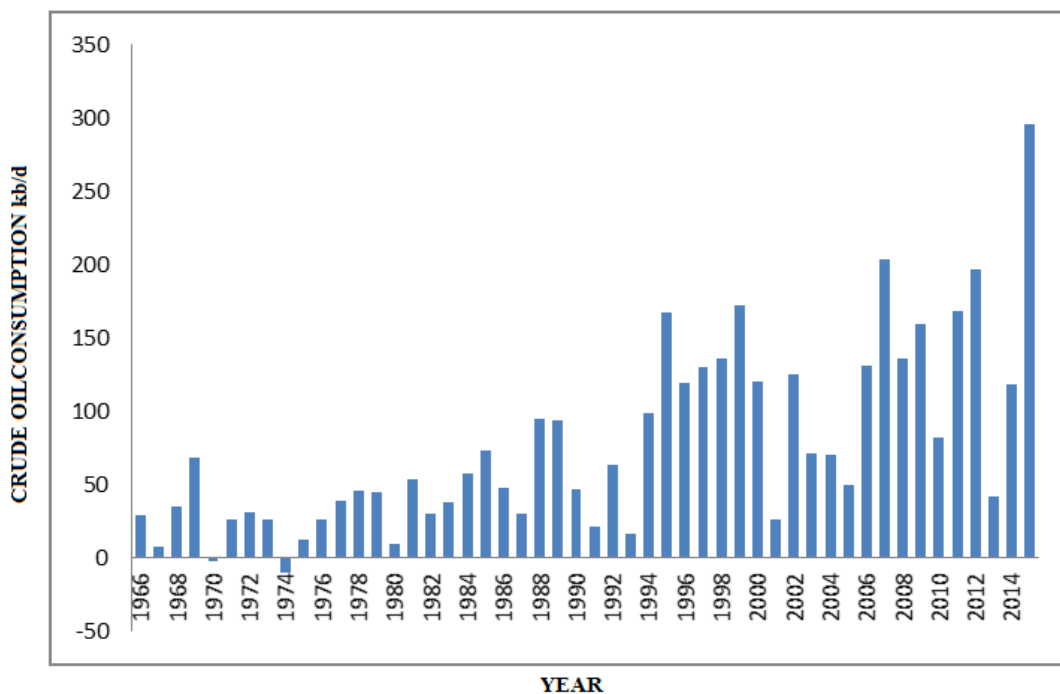

Fig-1: Consumption of Crude Oil 2014 [1].

2. MATERIALS AND METHODS

Lithium-substituted magnesium ferrite pellets were synthesized by solid state reaction method. High-purity precursors $MgCO_3$, Li_2CO_3 and Fe_2O_3 were taken in 0.8:0.1:1 molar ratio [6]. This ratio of magnesium and lithium had exhibited highest sensitivity for water vapour sensing reported [7]. Precursor powders were mixed and grinded for 2 h in pestle and mortar. Fine powder was calcined at 850 °C for 10 h in air. Calcined powder was grinded for 30 min and pressed in to a $2.2 \times 2.2 \times 0.1$ cm3 pellet and 4.6 cm diameter circular pellet of 0.1 cm thickness. Subsequently, the pellets were sintered at 1050 °C for 6 h in air. Comb patterned silver electrode of 0.1 μm thickness was sputtered on one face of a square pellet, and the other face of the pellet was covered with a 0.3-mm thick zinc plate. Similarly, a circular pellet was fabricated into a bigger cell. The synthesized pellets and electrode scheme on pellet are shown in Fig-2.
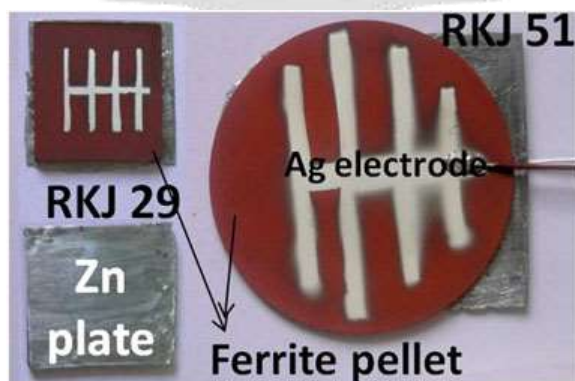

Fig-2: Showing the actual Hydroelectric Cell (HEC) [7].

3. WORKING OF HYDROELECTRIC CELL

Li-substituted Magnesium ferrite has been processed in such a way to create oxygen deficiency and nanoporous microstructure in it [7]. Magnesium ferrite is a ternary spinel compound, non-stoichiometric in oxygen inherently present in spinel structure due to imbalance in oxygen and cation components [8]. At high temperature under reductive atmosphere ferrite have the tendency to form non-stiochiometric compounds without degradation of spinel structure [9].

In the synthesis of Li-substituted magnesium ferrite, carbonates of magnesium and lithium provide some reductive atmosphere during calcination process. Magnesium ferrite is an oxygen deficient porous material processes large specific surface area and high electrical resistance of order of $10^8\Omega$. Also 20% divalent magnesium ion has been replaced by monovalent lithium ions that create more oxygen vacancy in the spinel structure. Oxygen vacancies trap the electrons and aggregate the electric charge [10]. These electric charges pull the oxygen of polar water molecule and dissociate it into hydroxide ion and proton.
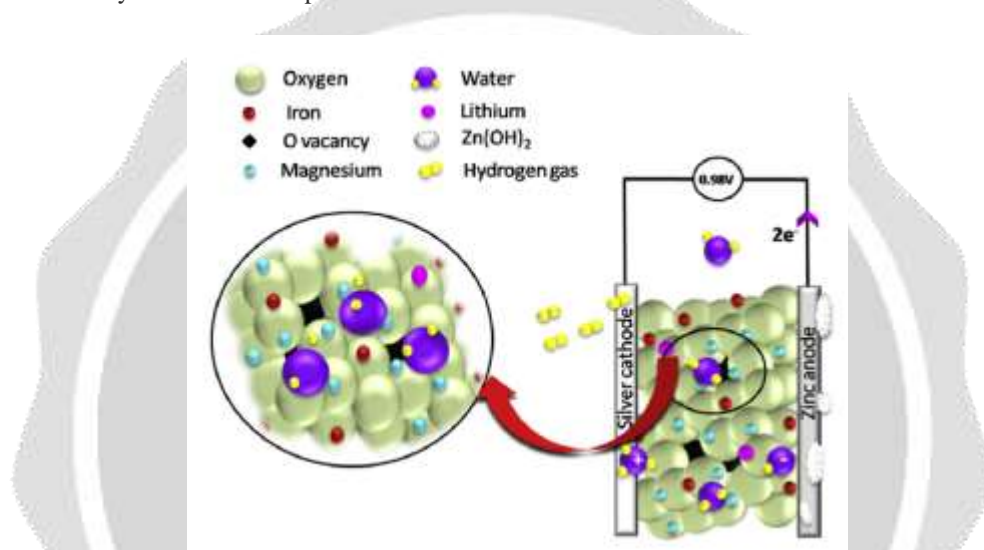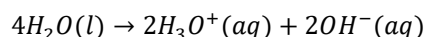

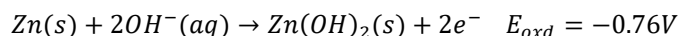**Fig-3**: Working of Li-substituted magnesium ferrite

In addition, surface cations Mg, Li and Fe provide unsaturated bonds due to termination of periodic lattice which chemidissociates water molecules as shown in figure 3. The chemidissociation process takes places in the 3-dimensional network of nanoporous microstructure of ferrite. On dissociation surface OH⁻ ions water molecule get physiorbed and protons via hydrogen bonded water molecule. Protons traped inside the nanopores, resulting subsequently generate electric field inside the pore resulting into further dissociation of physisorbed water molecules.

Ferrite pellet synthesis processing processing has been engineered in such a way that unsaturated surface cations, oxygen vacancies and nanopores have been created and utilized for chemidissociation of water molecules at room temperature. Subsequently, electrical energy has been generated by incorporating Zn and Ag electrodes on ferrite pellet to obtain voltage and current by oxidation/reduction reaction.
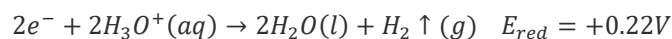
Water molecule dissociation at Li-magnesium ferrite

$$4H_2O(l) \rightarrow 2H_3O^+(aq) + 2OH^-(aq)$$

At Zinc electrode (anode)

$$Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^- \quad E_{oxd} = -0.76V$$

At silver electrode (inert cathode)

$$2e^- + 2H_3O^+(aq) \rightarrow 2H_2O(l) + H_2 \uparrow (g) \quad E_{red} = +0.22V$$

Overall Cell Reaction
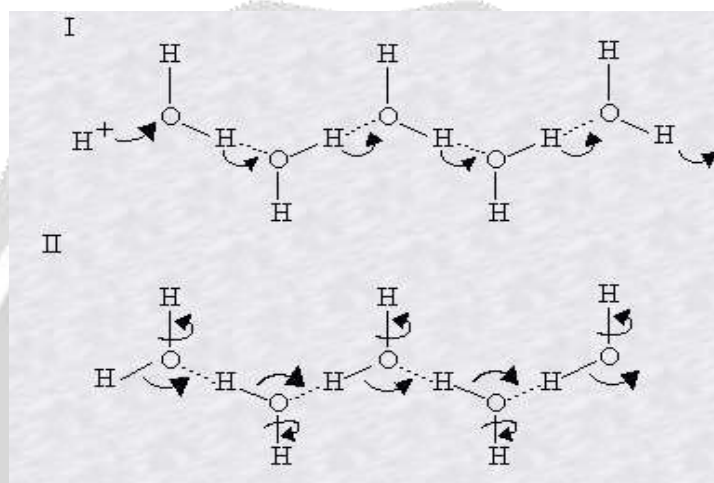$$Zn(s) + 2OH^-(aq) + 2H_3O^+(aq) \rightarrow Zn(OH)_2(s) + 2H_2O(l) + H_2(g) \uparrow \quad E_{cell} = 0.98V$$

4. GROTTHUSS CHAIN REACTION

Water is a good conductor of protons, because of the H-bonded networks between water molecules, that give water its liquid properties in the physiological range. Conduction occurs through a "hop-turn" mechanism, first suggested by Grotthuss, and often referred to as the Grotthuss mechanism.


Fig-4: Showing the Grotthuss Chain Mechanism for H$^+$ photon.

In the "hop" part of the mechanism, a proton first hops from the end of the H-bonded chain to an adjacent group (I, right) as shown in fig-4. Transfer of H-bond strength then allows it to be replaced by a H$^+$ binding at the other end, to give the structure in II. In the "turn" phase, rotation of the waters as shown in II then restores the starting structure (I) as shown in fig-4. In this H-bonded chain, the waters can in principle be replaced by suitable protein side chains with H-bonding potential.

5. GIBB'S FREE ENERGY AT LI-SUBSTITUTED MAGNESIUM FERRITE

Dissociated of water molecule occurs on ocatahedrally unsaturated surface cations and oxygen vacancies created by lithium substitution in magnesium ferrite. Lower synthesis temperature of ferrite has generated nanopores in ferrite network towards attached Zn and Ag electrodes. When HEC is partially dipped in deionized water, spontaneously hydroxide (OH$^-$) and hydronium ions (H$_3$O$^+$) are produced by water molecule dissociation. The reaction take place is given below:

$$2H_2O(l) \leftrightharpoons OH^-(aq) + H_3O^+(aq)$$
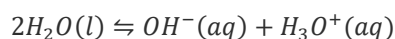
Gibb's free energy at room temperature (25 °C) of above chemical reaction is

$$\Delta_r G^°(25°C)_{Eqn.} = -2\Delta_f G^°_{H_2O(l)}(25°C) + \Delta_f G^°_{OH^-(aq)}(25°C) + \Delta_f G^°_{H_3O^+(aq)}(25°C)$$
$$= -2(-237.13 \text{ kJ/mol}) + (-157.24 \text{ kJ/mol}) + (-237.13 \text{ kJ/mol})$$
$$= 79.89 \text{ kJ/mol}.$$

From above chemical reaction, this much energy (79.89 kJ/mol) take place from atmosphere through Li-substituted Magnesium ferrite. It is n-type semiconductor, electron are majority carries and holes are the minority carries.

Diffuse reflectance spectra of dry ferrite powder have been performed for calculating optical band gap. Diffuse reflectance spectra of ferrite powder are shown in Figure 5. Band gap E_g of ferrite has been obtained by point of intersection between linear fit on $[F(R).h\upsilon]^2$ at Y-axis and photon energy on X-axis[11].
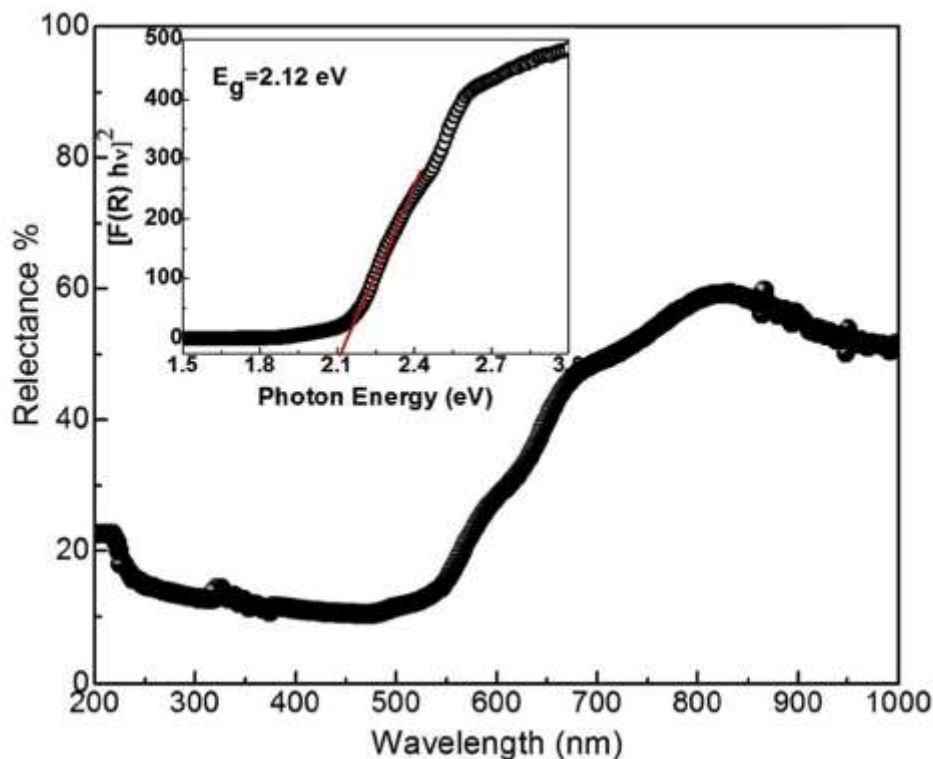
Fig-5: Showing Reflectance % (diffuse reflectance) vs. UV-Vis wavelength of Li-magnesium ferrite, Kubelka-Munk transformed reflectance spectra of ferrite showing band gap E_g in inset [11].

The optical band gap of Li-magnesium ferrite have been determined by diffuse reflectance using Tauc equation:

$$(\alpha h\vartheta)^n = A(E - E_g)$$

Where α is absorption constant,
   A is constant,
   E =hυ is photon energy,
   E_g is the band gap energy, and
   n = 2 for direct transitions.

Absorption coefficient is a derivate of Beer Lambert Law

$$l = l_0 * \exp(-\alpha d)$$
$$1 = \frac{l_0}{l\exp(\alpha d)}$$
$$\exp(\alpha d) = \frac{l_0}{l}$$
$$\alpha = \frac{\ln(\frac{l_0}{l})}{d}$$
$$\alpha = 2.303\frac{A}{d}$$

Where α = absorption Coefficient,
     d = thickness (cm),
     l_0 = incident intensity,
      l = transmitted intensity,
   A =absorbance = log (l_0/l),

In diffuse reflectance, F(R) is proportional to α and Tauc equation is written as:

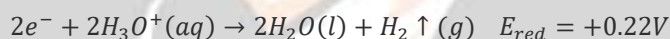$$[F(R).h\vartheta]^2 = A(E - E_g)$$

Optical band gap has been estimated by extrapolating tangent to maximum flat portion of $[F(R).h\upsilon]^2$ slope that intersected photon energy on X-axis at 2.12 eV [12].The direct band gap value for magnesium ferrite has been reported between 2.0 and 2.4 eV [13]. This band gap value reveals that there is no significant change by lithium substitution in magnesium ferrite. It also confirms Li-magnesium ferrite cannot absorb UV-visible photon energy directly, hence the possibility of dissociation of water molecule by visible photon is negligible.

6. GIBB'S FREE ENERGY FOR HYDROELECTRIC CELL (HEC)

 Voltage is generated by oxidation reaction occurring at Zn electrode as:-

$$Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^- \quad E_{oxd} = -0.76V$$
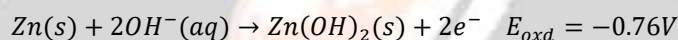
Reduction of H_3O^+ occurring at Ag electrode as H_2 gas evolution by accepting electrons from Zn electrode through external circuit:-

$$2e^- + 2H_3O^+(aq) \rightarrow 2H_2O(l) + H_2 \uparrow (g) \quad E_{red} = +0.22V$$

Overall Cell Reaction

$$Zn(s) + 2OH^-(aq) + 2H_3O^+(aq) \rightarrow Zn(OH)_2(s) + 2H_2O(l) + H_2(g) \uparrow \quad E_{cell} = 0.98V$$

Overall Cell Potential

$$\Delta E_{cell} = E_{red} - E_{oxd} + \frac{RT}{nF}\left[2.303log\frac{[H_2O]^2}{[Zn(OH)_2]}\right]$$

Where concentration of $Zn(OH)_2$, H_2O is equal to 1
.

$$\Delta E_{cell} = 0.22 - (-0.76) + 0$$
$$\Delta E_{cell} = 0.98\,V$$

We know that

$$\Delta G = -nF\Delta E_{cell}$$

Where n = number of electron transfer,
     F = Faraday's Constant = 96.5 KJ/mol,

$$\Delta G = -(2)(96.5)(0.98)KJ/mol$$
$$= -189.14\,KJ/mol$$

In Hydroelectric Cell (HEC), as ΔG is -189.14 KJ/mol means spontaneous chemical reaction.

7. CONCLUSION

In HEC, cell current and voltage generation has been achieved by water molecule dissociation on octahedrally coordinated unsaturated suface Mg, Li ions and oxygen vacancy created by lithium substitution in magnesium ferrite

at room temperature. Hydronium ions trapped in the nanopores of ferrite develop enough electric field to dissociate physisorbed water molecules spontaneously. Ferrite pellet synthesis processing processing has been engineered in such a way that unsaturated surface cations, oxygen vacancies and nanopores have been created and utilized for chemidissociation of water molecules at room temperature. Subsequently, electrical energy has been generated by incorporating Zn and Ag electrodes on ferrite pellet to obtain voltage and current by oxidation/reduction reaction. The process of water molecule dissociation is accelerated in a bigger way because of nanonpores to increase current in the cell. HEC is cost effective, completely safe, non-polluting alternative to portable green energy source. Moreover, the role of nanoporous magnesium ferrite pellet as proton exchange membrane in fuel cell would be highly beneficial.

8. REFERENCES

[1]. Meise P., 2014, "Overview of Renewable Energy Potential of India", *Energy Aspect of India.* Crude   oil Consumption.

[2].Wei D. Writable electrochemical energy source based on graphene oxide. Scientific Reports 2015; 5:15173. doi:10.1038/srep15173.

[3]. Miljkovic N, Preston DJ, Enright R, Wang EN. Jumping-droplet electrostatic energy harvesting. Applied Physics Letters 2014; 105:013111. doi:10.1063/ 1.4886798.

[4]. Meng Q, Kenayeti Y, Chung DDL. Battery in the form of a cement-matrix composite. Cement and Concrete Composites 2010; 32:829. doi:10.1016/j.cemcon comp.2010.08.009.

[5]. Byrne A, Holmes N, Norton B. Cement based batteries and their potential for use in low power operations. Materials Science and Engineering 2015; 96:012073. doi:10.1088/1757-899X/96/1/012073.

[6]. Kotnala R K., Shah J., 2016, "Green hydroelectric energy source based on water dissociation by nanoporous ferrite", International Journal of Energy Research, doi: 10.1002/er.3545.

[7]. Shah J., Jain S., Shukla A., Gupta R., Kotnala R K., 2017, "A facile non-photocatalytic technique for hydrogen gas production by hydroelectric cell", International Journal of Hydrogen Energy, Vol:xxx(2017), pp:1-7.

[8]. Paladino AE, 1963, "Phase Equilibria in the Ferrite Region of the System FeO-MgO-Fe_2O_3", J Chem Phys, Vol:39, pp:435-439.

[9]. Kojima M., Sano T,Wada Y, Yamamoto T, Tsuji M,Tamaura .Y, 1963, J phys Chem Solids,Vol:57(11), pp:1757-1763.

[10]. Schaub R, Thostrup P, Lopez N, Laegsgaard E, Stensgaard I, Norskov JK, 2001, "Oxygen Vacancies as Active Sites for Water Dissociation on Rutile $TiO_2(110)$", Phys Rev Lett, Vol:87(26), pp:266104.

[11]. Shah J., Jain S., Shukla A., Gupta R., Kotnala R K., 2017, "A facile non-photocatalytic technique for hydrogen gas production by hydroelectric cell", International Journal of Hydrogen Energy, Vol:xxx(2017), pp:1-7.

[12]. Koferstein R., Walther T., Hesse D., Ebbinghaus S., 2013, "Preparation and characteristics of nanosized magnesium ferrite powders by a starch-gel process and corresponding ceramics", Vol:48(2013), pp:6509-6516.

[13]. Loanathan A., Kumar K., 2015, "Effects on structural, optical and magnetic properties of pure and Sr-substituted $MgFe_2O_4$ nanoparticles at different Calination temperatures, Application Nanoscience, Vol:6, pp:629-639.