Substitution in Titanium Dioxide Hydroelectric Cell Induces Higher Green Energy

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Abstract -- **Hydroelectric cell (HEC) is a path-breaking invented device producing electricity by water dissociation using specially processed metal oxides. In this work, effect of Li/Mg/Fe substitution in titanium dioxide is explored. Molar ratio of substituent and TiO_2 is taken 0.1:0.9. One inch square pellet of powder was palletized by hydraulic press and samples were synthesized by solid state reaction method. Hydroelectric cell was fabricated by attaching two dissimilar electrodes zinc and silver on opposite face of square pellet. When few drops of water are sprinkled on HEC surface, it instantly dissociates water into OH- and H+ ions without use of any external source. Dissociated ions move toward zinc and silver electrodes and form zinc hydroxide and hydrogen. Due to redox reactions, potential develops in the cell and current flows in external circuit. Magnesium-substituted TiO2 generates maximum short circuit current 6 mA and open cell-voltage 0.925 V. Magnesium substitution increased the porosity of TiO2 thus enhanced exposed surface area in TiO2 for more water molecule dissociation, which ultimately enhances current in the cell.**

Indexing Terms: *Hydroelectric cell, Molecular dissociation, Magnesium substitution, Titanium dioxide, Nanopores, Surface reactivity*

I. INTRODUCTION

RECENTLY, population growth and industrial development surged energy demand. New energy sources should fulfill the criteria of easy availability and be environment-friendly. Researchers are looking towards sustainable energy modes due to consumption or utilization of energy demands protection of environment [1]. So far in the quest of industrial and economic development, its dreadful side has been ignoring the environment which is getting worse day by day. The time has come when a deep thought process as well as strictaction is required to save the planet [2]. Recently invented green energy device Hydroelectric cell (HEC) is the exceptional example of sustainable energy source. It produces electricity by dissociation of water molecules at unsaturated surface cations and oxygen vacancies on ferrite/oxide surface. In this device, initially water molecules are chemi-dissociated on oxygen deficient porous surface of the material followed by physi-dissociation of water molecules at nanopores due totrapped ions create electric potential inside nanopores [3]. At inert cathode, hydrogen gas is liberated and on anode, zinc hydroxide is formed due to redox reaction [4,5]. Several metal oxides have been extensively explored and converted for hydroelectric cell application [6].

Metal oxides exhibit oxygen defects in crystal structure making its surface reactive towards other molecules like water, microorganisms and gases etc [7-9]. Their surface reactivity qualifies them more suitable for various sensors application, antibacterial agent and catalyst support [10-12]. Particularly, by controlling processing conditions its reactivity can be improved which is the basic requirement for water molecule chemi-dissociation in hydroelectric cell. Titanium dioxide is naturally occurring oxide of titanium and it mostly occurs as a mineral in rutile and anatase. Its rutile phase is thermodynamically most stable form and has highest refractive indices at visible wavelengths. It has got wide range of applications including in paints, cosmetics, plastics, glazes, tooth paste and food coloring [13-16].

Titanium dioxide has been explored widely for its photo catalytic activity and water splitting property. The process requires excitation of titanium dioxide by electromagnetic radiation in ultra violet region (band gap of 3.2eV) and feebly excited by visible light. Excitation generates electron hole pair which splits water, however, the process has drawback, like recombination of electron and hole occur very rapidly at the scale of 10 ns causes low efficiency of process and moreover reaction also takes place in backward direction [17,18]. Therefore studies are focused to the modification of TiO_2 for the enhancement of photocatalytic reaction [19-21]. In this paper effect of Li/Mg/Fe substitution in titanium dioxide on water molecule dissociation for current and voltage generation by hydroelectric cell has been investigated. In hydroelectric cell water splitting majorly takes place at defect sites of porous material without applying any external energy and splitted ions have been easily collected at respective electrodes. Pure titanium dioxide has previously been reported as a potential candidate for HEC [5]. This paper investigates the effect of alkali, alkaline earth and transition metal substitution in titanium dioxide on current and voltage

generation by hydroelectric cell.

II. MATERIAL AND METHODS

Analytical grade precursor powder of titanium dioxide, magnesium carbonate, lithium carbonate and iron oxide were taken for the synthesis of substituted titanium oxide. Substituted TiO_2 samples of hydroelectric cell were synthesized by solid state reaction method. Lithium substituted titanium oxide was synthesized by mixing magnesium carbonate and titanium oxide precursor powder in molar ratio 0.1:0.9 followed by grinding in a pestle mortar for 40 minutes. For magnesium and iron substitution in titanium oxide similar molar ratio and grinding method was used. The grinded powders were pre-sintered at 800 ^oC for 2 hrs. Pre-sintered powders were again grinded for 30 minutes and pressed into 2.5x2.5x0.1 cm^2 pellet. For reference, pure titanium dioxide grinded powder was also pre-sintered and pelletized. These pellets were finally sintered at 1000 ^oC for 2 hrs. Comb patterned silver cathode of 1 μm thickness was screen printed on one face of all pellets while the opposite face was covered with a 0.3 mm thick zinc plate as anode. Conducting wires were soldered on both electrodes and the current and voltage outputs were taken by using a current source meter and multimeter. The experimental setup for measuring V-I performance is shown in figure 1.

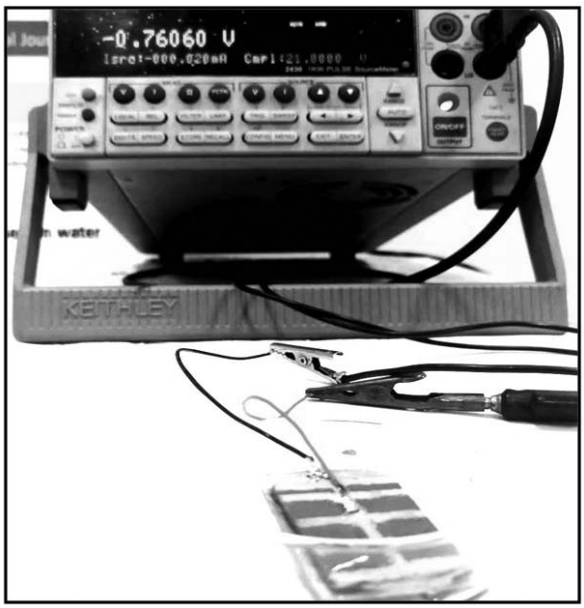

Figure 1. Experimental set-up for measurement of V-I polarization of hydroelectric cell (HEC is at the bottom).

III. RESULTS AND DISCUSSION

Current and voltage response from all the samples has been shown in Table 1. Initial chemi-dissociation of water molecules on defective nanoporous TiO_2 followed by physisorption of water layers provide conducting path for proton hopping. Hopping protons get trapped inside the nanopores provide high electric charge potential to dissociate further water molecules. Electricity is generated by hydroxide migration via grain boundaries and protons through hopping get captured by zinc and silver electrodes. It is clear from the table l that by lithium substitution in titanium dioxide increased the current 3.2 mA compared to 2.3 mA in pure titanium oxide while the voltage remains same. It may be due to monovalent lithium ion (0.78 Å) bigger than tetravalent titanium ion (0.67 Å) creates deformation in TiO_2 lattice, preferably occupy interstitial sites and accumulated at the surface forming lithium rich phase [22]. Deformation in TiO_2 lattice created oxygen vacancies V_o in the lattice. Li^+-V_o pairs attract polar water molecules more closely to the surface leads to chemi-dissociation. Thus current increased in due to increased water molecules dissociation. Divalent magnesium substitution increased the current as well as voltage to 6.0 mA and 0.925V respectively. Magnesium ion (0.76 Å) substitution in TiO_2 also induces strain in the lattice due to larger ionic radii. Magnesium substitution increases the porosity of TiO_2 due to fast thermal expansion consequently increases the surface area of TiO_2 [23]. Large surface area increases the reaction sites for water on TiO_2 surface [3]. A schematic diagram representing water molecule dissociation and electricity generation by hydroelectric cell shown in figure 2.

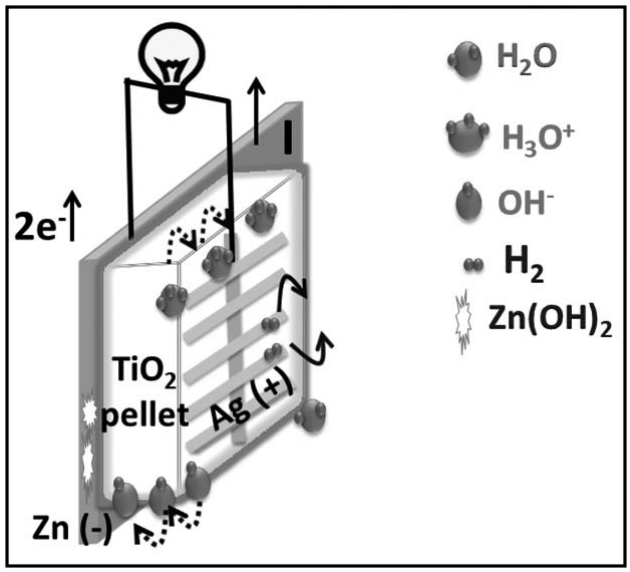

Figure 2. Working mechanism of water molecule dissociation by TiO_2 and electricity generation by hydroelectric cell.

Thus surface Mg^{+2}-V_o pair in large amount exposed on TiO_2 surface due to increased porosity. Hence more water molecules are strongly attracted towards Mg-TiO_2 surface. On the other hand cell fabricated from iron substituted titanium oxide reduced current as well as voltage. Current reduced to about 4.5 times and voltage dropped to 0.725 from 0.90 V. Reduction in cell voltage may be due to oxidation of Fe^{2+} to Fe^{3+} ion forming internal cells and impeding OH^- ion diffusion towards Zn electrode and hence reducing the current.

TABLE 1 -- PROCESSING CONDITIONS AND CURRENT–VOLTAGE RESPONSE OF THE HEC SYNTHESIZED FROM TITANIUM DIOXIDE SAMPLES

Sample	Max. current output (mA)	Max Voltage Output (V)
TiO_2 bare	2.3	0.90
Li-TiO_2	3.2	0.90
Mg-TiO_2	6.0	0.925
Fe-TiO_2	0.5	0.725

IV. CONCLUSION

Hydroelectric cells of Li, Mg and Fe substituted titanium dioxide have been fabricated. It has been observed that Li and Mg substitution in TiO_2 increased the cell current while substitution of Fe decreased the cell current drastically. It has been analyzed bigger fixed valance state Li^+ and Mg^{2+} ions induces the strain in TiO_2 structure and increased oxygen vacancies. Metal ion and oxygen vacancy pairs attracted and dissociated more water molecules thus enhance the cell current. Thus alkali and alkaline earth metal are the best suited substitutes in order to create defects and porosity in TiO_2 to achieve enhanced green electricity.

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Dr. Jyoti Shah former DST-Women Scientist along with 15 years of research experience is one of the inventors of green energy source "Hydroelectic cell" in 2016.
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