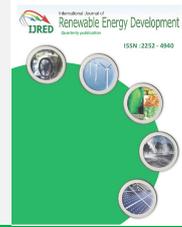




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Research Article

Evaluating the Materials Used for Hydrogen Production Based on Photoelectrochemical Technology

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ABSTRACT. Hydrogen as a CO₂-free fuel has been considered as a serious alternative for problematic fossil fuels in recent decades. Photoelectrochemical (PEC) water splitting is a developing solar-based technology for hydrogen production. In this study, some possible options for upgrading this technology from R&D stage to prototype stage through a material selection approach is investigated. For these purposes, TOPSIS algorithm through a multi criteria decision making (MCDM) approach was utilized for evaluating different (PEC)-based hydrogen production materials. TiO₂, WO₃ and BiVO₄ as three semiconductors known for their PEC application, were selected as alternatives in this decision-making study. After defining a set of criteria, which were assessed based on similar studies and experts' visions, a group of ten PEC-experts including university professors and PhD students were asked to fill the questionnaires. The eight criteria considered in this study are include "Study Cost", "Synthesis Simplicity", "Facility & Availability", "Deposition capability on TCO", "Modifiability", "Commercialization in H₂ production", "Physical and Chemical Durability" and "Eco-friendly Fabrication". The final TOPSIS results indicates that TiO₂ is selected as the best semiconductor for further investments in order to upgrade the PEC-based hydrogen production technology from R&D level to prototype stage. ©2019. CBIORÉ-IJRED. All rights reserved

Keywords: MCDM, TOPSIS, Hydrogen generation, PEC, Semiconductor.

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1. Introduction

As the most important future energy carrier, hydrogen (H₂) has drawn a considerable attention and is created a vital demand for H₂ production technology investment. Hydrogen can be used as fuel for engines and fuel cells to increase efficiency and decrease the environmental issues (Muppala, Manickam, & Dinkelacker, 2015; Talukdar, 2017). There are several approaches for producing hydrogen (Amekan et al. 2018; Kanoglu, Yilmaz, & Abusoglu, 2016). Due to advantages of renewable energy systems especially lower carbon dioxide emission (Bardineh et al. 2018), these types of technologies is more preferable for producing hydrogen. The Photoelectrochemical (PEC) method is one of the cleanest developing technologies which is capable of producing H₂ gas by utilizing water (Ali et al. 2018; Chen et al. 2013; Chen et al. 2018). Apart from that, this technology has applications in water treatment industries, making it a promising technology for the near future (Mills & Le Hunte, 1997).

The PEC technology is based on utilizing a semi-conductive material to absorb sun-light and use it as the driving force of a number of reactions, including water splitting and degradation of some water organic pollutants. In these technologies, sun-light produces pair

electron/hole in the semiconductor causing an oxidation–reduction reaction from water to obtain hydrogen and oxygen separately. A schematic description of a photoelectrode-based PEC devise is illustrated in Figure 1.

Being in the R&D stage, PEC has yet to find a way to produce hydrogen in large scale. Additionally, in comparison with current hydrogen production techniques, the efficiency of PEC method is insignificant. However, among various hydrogen production technologies, PEC is considered as one of the cleanest, as it only relays on solar energy and water molecules to produce hydrogen. Besides the improvement of its efficiency has been remarkable in the past decade. Therefore, this technology is considered as an important option for replacing troublesome fossil fuels in hydrogen system in near future.

International organizations of energy have recognized the importance of PEC technology in the future of hydrogen production technologies. According to the renewable hydrogen production pathways presented by International Renewable Energy Agency (IRENA) (IRENA, 2018), solar based hydrogen production technologies such as PEC are in the applied research stage of the pathway. Figure 2 shows the current maturity levels of renewable hydrogen production technologies. The U.S. Department of Energy (DOE) has published a list of

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technical targets for PEC-based hydrogen production technologies (described later in "Literature review" section). In This list two type of PEC technology are considered: 1) Photo-electrode systems and 2) photo-

catalysis systems (U.S. Department of Energy [DOE], 2018).

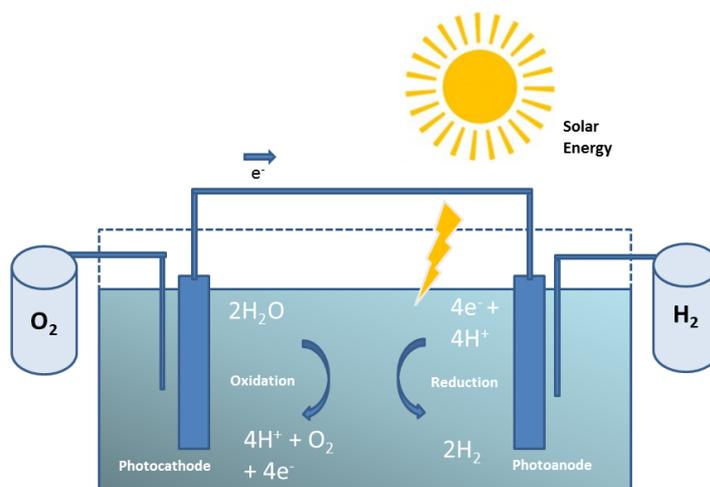


Figure 1. A schematic description of a photoelectrode-based PEC devise

Therefore, for PEC-based technologies, which are in the R&D phase of H₂ production, one of the essential questions is, what material should be invested on, to reach the prototype level and in this regard increase the chance of its commercialization in the shortest time. To find the answer, considering the advantages and disadvantages of materials to each other in various areas, it is needed to utilize a decision-making process. Among the materials used in renewable hydrogen production technologies, n-type semiconductor materials such as TiO₂, WO₃, Fe₂O₃ and BiVO₄ are used for PEC technology due to their suitable physical and chemical properties such as suitable

band gap, however, each semiconductor has advantages and disadvantages over others. Low light-absorption efficiency, electrical and quantum efficiency are some technical features of semiconductors, while factors such as availability, modifiability, research and experiment costs, safety and eco-friendliness all are features which affects the capability of a material to reach the prototype level in the fastest and safest way. The variation of these criteria brings the necessity of utilizing a decision-making procedure.

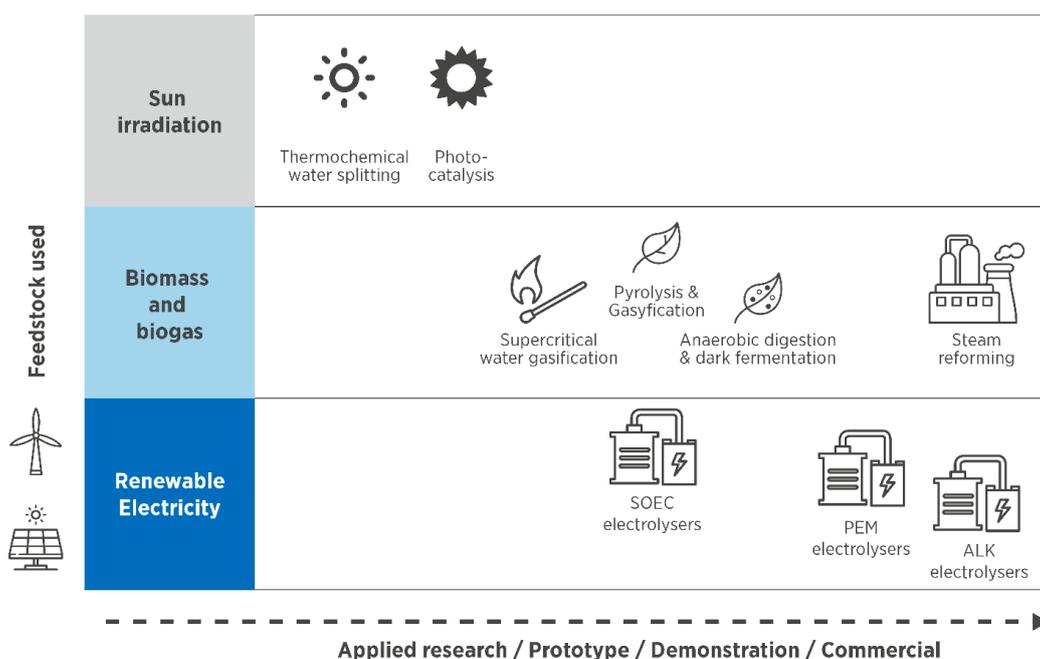


Figure 2. Current levels of maturity for renewable hydrogen production technologies (IRENA, 2018)

The most suitable semiconductor for PEC technology can be decided through different methods. Though for all of these methods, the first and one of the most important steps is to define the genuine criteria and to classify their importance properly. Economic issues, facility, environmental considerations, availability and commercialization capability are some of the most frequent criteria in R&D project evaluation and technology selection decision makings (Vafaeipour et al. 2014; Wang et al. 2015; Watson & Hudson, 2015; Zhao & Li, 2015).

In this study, for the first time, the comparison is carried out between TiO₂ and WO₃, as the two well-known semiconductors, and BiVO₄, as a semiconductor that is attracting a growing attention, through a multi-criteria decision making (MCDM) approach. In this research, first a set of criteria are defined and then evaluated by PEC experts via a designed questionnaire. The criteria include "Study Cost", "Synthesis Simplicity", "Facility & Availability", "Deposition capability on TCO", "Modifiability", "Commercialization in H₂ production", "Physical and Chemical Durability" and "Eco-friendly Fabrication". Finally, by utilizing TOPSIS algorithm the best semiconductor is selected. The goal of this work is to propose a new approach for deciding about available alternatives in progressing a technology. Here the case is to find the best semiconductor in order to help the PEC technology (which is in the R&D level) reach to its next step (prototype level) considering the aforementioned criteria.

2. Literature Review

Excessive use of fossil fuels has caused an increasing rate of CO₂ emission in recent years. On the basis of BP report (BP, 2018), the emission of carbon dioxide has noticeably increased from 18364.1 Mt in 1980 to approximately 33444 Mt in 2017. The trend of carbon dioxide emission during the mentioned years is represented in Figure 3.

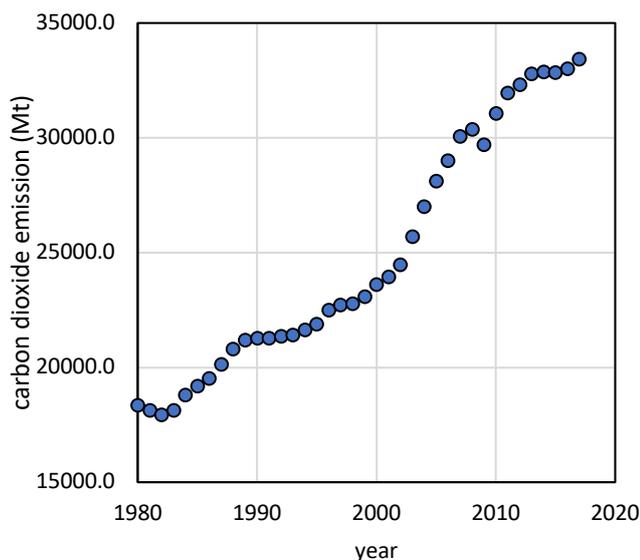


Figure 3. Carbon dioxide emission in recent years (Bp, 2018)

Solving the CO₂ emission problem of fossil fuels requires either an improvement in their efficiencies (Ahmadi et al. 2018a; Ramezanzadeh et al. 2018a) or

replacing them with other energy resources (Ghoujdi, 2018, Ahmadi et al. 2018b; Ahmadi et al. 2018c; Ahmadi et al 2018d). One of the fossil fuel applications which can be replaced by renewable energies is hydrogen production (Ahmadi et al. 2018d; Amekan et al. 2018; Handayani & Ariyanti, 2012; Madvar et al., 2018; Menges & Pfaffenberger, 2015; Kaloï 2017). There are various ways and diverse energy sources to produce this gas. Fossil fuels and a wide range of renewable energies can be utilized in H₂ production processes. Currently, the main source used for hydrogen production is natural gas, which has 48% share; while applying electrolysis has the lowest share with 4%. The shares of each sources in produced hydrogen is shown in Figure 4.

As mentioned earlier, one of the most attractive technologies of hydrogen industries is PEC technology. PEC is known as a solar-based technology which directly uses the abundant energy of sun. DOE considers PEC technology as one of the elements of their long-term program in hydrogen production prospect (U.S. Department of Energy [DOE], 2017). Figure 5 shows a broad view of this prospect. As it is illustrated in this portfolio, PEC technology is planned to be one of central sources of hydrogen along some technologies such as natural gas reforming, gasification and electrolysis. The plant capacity targeted for the PEC technology is in scale of generating 50000 kg hydrogen per day. In this program the timeline is divided into near-term, mid-term and long-term periods and PEC belongs to the solar pathways which is anticipated for the long-term program.

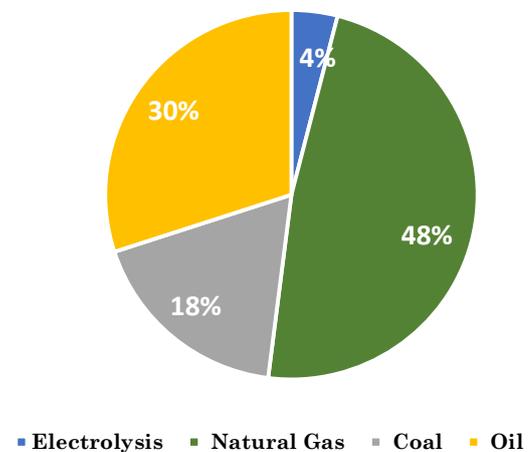


Figure 4. Share of various sources in produced hydrogen (IRENA, 2018)

DOE has set targets for PEC technology in H₂ production. The targets are generally about three main topics: 1- the production cost, 2- The technology efficiency and 3- The replace time of PEC parts. The two considered types of PEC technology in this report include photoelectrode-based and photocatalyst-based PEC devices. The five targets of DOE for photoelectrode system are as follows:

- 1- Cost of PEC-based generated hydrogen
- 2- Concentrator and PEC receiver capital cost
- 3- Annual cost of electrode
- 4- Solar to hydrogen energy conversion
- 5- Hydrogen production rate of 1-sun radiation

These targets are set for years 2011, 2015 and 2020 in order to be a set point especially for the long-term researches in PEC field. While there is also an ultimate target presented by DOE which is targeting the market competitiveness ([DOE], 2018).

DOE's Fuel cell technologies office has described their plan for diverse hydrogen production technologies in their multi-year research, development and demonstration plan. As it is reported, following timeline for PEC technology development is established (U.S. Department of Energy [DOE], 2015):

- 1- Establishing standards for all aspects of the PEC technology.
- 2- Improving durability in PEC devices with high-efficient materials.
- 3- Improving efficiency in PEC devices with stable materials.
- 4- Discovering stable and highly efficient materials for PEC uses.
- 5- Developing cost-effective PEC-based water-splitting reactors.

PEC as a semiconductor-based hydrogen production technology, requires developments in materials to pass the early stages of developments (U.S. Department of Energy [DOE], 2015). There are numerous semiconductors which can be utilized as the main material of the PEC technology. DOE has divided current material systems for PEC photoelectrodes into three categories based on their characteristics and research challenges:

- 1- High efficient, relatively high cost, limited lifetimes (e.g., Group III-V crystalline materials)
- 2- Lower efficiency, relatively lower cost, stable (e.g., metal- and mixed-metal oxide thin films)
- 3- Hybrid and multi-junction systems

TiO₂, WO₃, Fe₂O₃, ZnO₂ and BiVO₄ are some of these alternatives all belongs to the second group. Materials of the second group due to their high stability and low cost, are more considerable option for further development. These semiconductors are developing and modifying through years and their cost, performance and durability are improving consistently. Metal and non-metal dopants, graphene, co-catalysts and variety of deposition methods are some means to enhance the performance and

endurance of PEC photoelectrodes. (Abe, 2011; Daghrir, Drogui, & Robert, 2013; Madhusudan et al 2013; Moniz, 2015; Ni et al. 2007; Zaleska, 2008).

However, in order to meet the objectives established by DOE in the shortest time, it is necessary to concentrate on a single material and invest all the time, money and energy assigned for the development project, on it. In this process the most important step is to select the best material for further investigation and investment. In this regard, the materials should be evaluated and a decision-making method should be utilized for the technology selection.

In order to find the best options, decision making algorithms have been widely used to find technology alternatives (Ghasempour et al. 2019). For example, Chang, et al (1994) have applied a fuzzy MCDM to select a strategy for technology transfer in biotechnology field. A technology selection algorithm using Data Envelopment Analysis (DEA) is proposed by Khouja to help potential buyers to choose a technology. It is a two phases algorithm which first identify technologies which matches vendors specifications and then the technology is selected using a multi criteria decision making model (Khouja, 1995). Using a strategic scorecard by Xia, et al is another example of decision-making application in the technology selection (Xia et al. 2017). Nazemzadegan et al (2017), compared Fuzzy, Linmap and TOPSIS decision making algorithms to find the best performance condition of a dish-Stirling engine in a multi-objective optimization program.

Research and Development (R&D) evaluation is also an example of employing decision making in technology selection. Eilat, et al (2008) through a multi-criteria approach have used the scorecard method alongside DEA to evaluate R&D projects. The study is useful in different life time of projects including the proposal step, in which the base and materials of the project should be decided. R&D evolution methods are divided into two main categories: 1- Weighting & Ranking methods and 2- Benefit-contribution methods (Poh, Ang, & Bai, 2001). The approach of the current study is through the Weighting & Ranking methods, as it is based on normalized weighted scores.

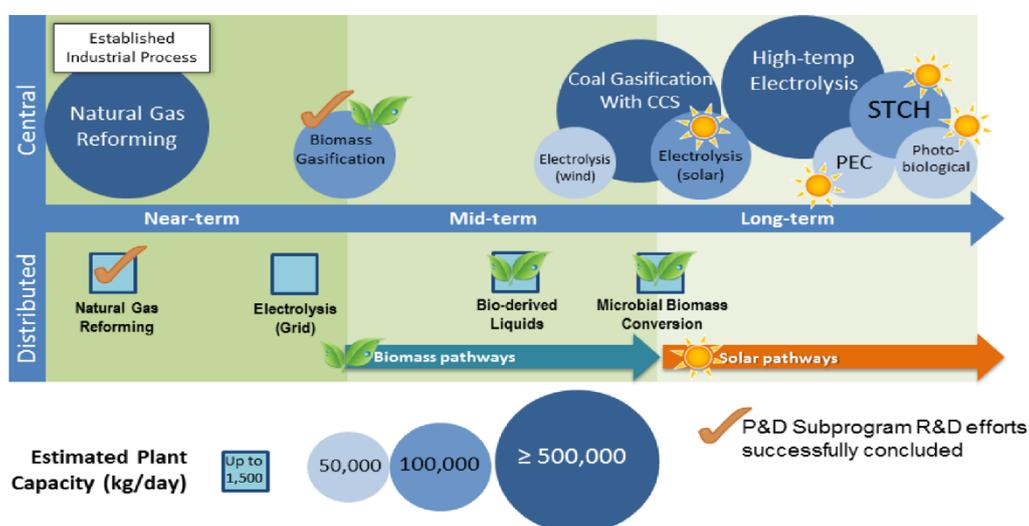


Figure 5. Broad hydrogen production prospect (U.S. Department of Energy [DOE], 2017)

3. Important Criteria affecting the PEC material selection

To start this decision-making procedure, a set of criteria needs to be arranged. Economic and environmental criteria are some frequent criteria used in many technology-based decision makings (Vafaeipour et al., 2014; Wang et al., 2015; Watson & Hudson, 2015; Zhao & Li, 2015). In addition to these criteria, there are criteria which usually are applied for R&D evaluation case studies. They include complexity, availability, growth potential, customer potential, etc. which all are factors for evaluating a project proposal attractiveness (Eilat et al., 2008; Victório, Costa, & Souza, 2015; Wang & Tang, 2015). Eilat et al, introduced their criteria in diverse perspectives including financial, customer, internal-business, learning & growth, uncertainty and resources (Eilat et al., 2008).

The criteria established in this study are generally a reflection of the photoelectrode production process. Therefore, photoelectrode as a PEC technology test sample, reflects the performance of the hydrogen generator final product. Similar to what it is reported in a PEC research proposal, through a photoelectrode preparation process there are steps can be sorted as follows:

- Gathering relevant information related to the process.
- Considering the location and facilities needed for the process.
- Providing precursor and other synthesis materials.
- Semiconductor Synthesis process and Modification (in case of necessity)
- Deposition process (on a TCO substrate)
- Physical and chemical stability tests
- Performance tests.

In order to overcome any mentioned stage properly, an uncertain amount of time, money and energy is required to spend. These requirements are so detail that are almost impossible to measure. In addition, there are unmeasurable factors such as complexity of the process, availability of the materials & facilities and product modifiability. Considering commercialization potential and Safety & Eco-friendly factor, which are two common criteria in R&D evaluation, these are all examples that are heavily depends on the expert's experiments.

So far a set of criteria has been established to facilitate the decision making process in order to conclude a semiconductor for PEC-based hydrogen generation. In addition to the literature review results, the PEC experts' Idea also has been considered in the criteria selection. Finally, the resulted criteria are categorized as follows:

- 1- Study Cost
- 2- Synthesis Simplicity
- 3- Facility & Availability
- 4- Deposition capability on TCO
- 5- Modifiability
- 6- Commercialization in H₂ production
- 7- Physical and Chemical Durability
- 8- Eco-friendly Fabrication

"Study Cost" refers to all cost of research phase of the project to achieve a test sample for the semiconductor. The test samples of semiconductors utilizing in PEC technology usually are their photo-electrodes. This criterion is one of the most important items in deciding a research proposal. Study cost cannot be determined just

by considering the price of precursor and synthesis materials. It is needed to predict up to the very last step of the synthesis and the tests to calculate the exact cost of the research, therefore a more practical approach to estimate the cost is to rely on experiences.

"Synthesis Simplicity" indicates the time, knowledge and experience needed for fabrication of the semiconductors' laboratory test samples. It is hard to predict how many hours a through experimental study will take, or how much literature should be investigated for a project or how much skill is needed to conduct the fabrication experiment; but on the other hand, it is possible to compare overall score of three different semiconductors in term of simplicity. 'Therefore, "Synthesis Simplicity" is one of the criteria of current study.

"Facility & Availability" refers to all laboratory facilities and the semiconductors' synthesis materials availability. To compare the synthesis procedure of the three semiconductors' photoelectrodes, the facilities and materials availability are factors that affects greatly the possibility of the procedure accomplishment. It is important to consider these two factors in the research proposal preparation in order to avoid any interval during the procedure.

"Deposition capability on TCO" implies that how facile, fast and in how many methods the layer of each semiconductor can be deposited on a TCO substrate. This factor is one of the most important elements in fabricating a semiconductor photo-electrode

"Modifiability" criterion is about the capability of each semiconductor in getting improved by using any modification method, including doping, making complexes, using co-catalysts, changing the assembly, etc. The more a semiconductor is modifiable, the more reliable it is, as it is more possible to find a way to improve its performance.

As a criterion, "Commercialization in H₂ production" is asking the experts that how many chances they predict for each semiconductor to get to the level of commercialization in the industry of H₂ production.

Durability of the fabricated Photoelectrode is one of the items included in the DOE target for PEC-based hydrogen production technologies. This item is considered in this study by "Physical and Chemical Durability" criterion. This criterion refers to durability of the fabricated photo-electrode as the test sample.

"Eco-friendly Fabrication" not only aims the safety and environmental aspects of final produced photoelectrode as the hydrogen production device, but also involves the fabrication procedure such as toxicity of precursors and solutions utilized through the synthesis process.

Considered criteria are set based on similar R&D evaluating and technology selection studies (Vafaeipour et al., 2014; S. H. Wang et al., 2015; Watson & Hudson, 2015; Zhao & Li, 2015) and all are assessed by three professionals in PEC field, before delivering questionnaires to the experts. The resultant score is normalized by TOPSIS method and after utilizing the decision-making algorithm, the best semiconductor is selected.

The overall procedure flowchart is illustrated in Figure 6. In the first step the importance weight of criteria is calculated based on experts' weight assessments. In the second step the normalized vector of alternatives is

calculated. Utilizing the weight vector of criteria, the normalized weighted vector of alternatives is achieved. In the next step TOPSIS decision making algorithm is applied to the normalized and weighted scores and resulted to final scores for semiconductors.

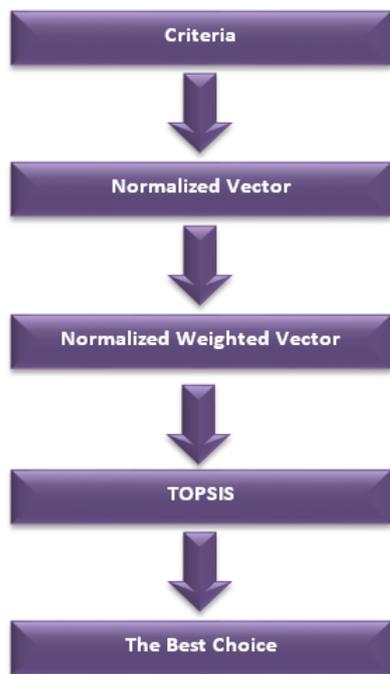


Figure 6. The decision making flow chart of current study

4. TOPSIS Method

The TOPSIS method, is a technique for ordering preferences based on similarity to the ideal solution. Some of the advantages of this method over other MCDM methods, such as ELECTRE, weighted product, and weighted sum, are its consistency and simplicity (El Amine et al 2014). TOPSIS also is known for its ability to consider a non-limited number of alternatives and criteria in the MCDM problems (Junior et al, 2014). By having these advantages TOPSIS has become one of the most regular MCDM methods (Tscheikner-gratl et al. 2017).

Utilizing an MCDM method, with m alternatives evaluated by n criteria, the data matrix can be considered as a $n \times m$ matrix where X_{ij} is the value for the i^{th} alternative determined by the j^{th} criterion. In first step, the normalized value should be calculated as (Nazari, Aslani, & Ghasempour, 2018):

$$r_{ij} = \frac{X_{ij}}{\sqrt{\sum_{i=1}^m X_{ij}^2}} \quad i = 1, \dots, m; j = 1, \dots, n \quad (1)$$

To obtain the weighted normalized vector, the score of each alternative should be multiplied by its weight as follows:

$$v_{ij} = w_j r_{ij} \quad (2)$$

Where, w_j is the weight of j^{th} criterion, resulted from dividing each criterion raw score to the linear average of all criteria's scores (Nazari, Aslani, & Ghasempour, 2018). For the j^{th} criterion, v_j^* and v_j^- represent the maximum and minimum weighted normalized values, respectively and are defined as:

$$v_j^* = \{v_1^*, \dots, v_j^*, \dots, v_n^*\} = \{\max v_{ij}\} \quad (3)$$

$$v_j^- = \{v_1^-, \dots, v_j^-, \dots, v_n^-\} = \{\min v_{ij}\} \quad (4)$$

In next step, for the i^{th} alternative, the distance of each criterion from, v_j^* and v_j^- , are calculated as (Nazari et al 2018):

$$S_i^* = \sqrt{\sum_{j=1}^n (v_{ij} - v_j^*)^2}, \quad i = 1, \dots, m \quad (5)$$

$$S_i^- = \sqrt{\sum_{j=1}^n (v_{ij} - v_j^-)^2}, \quad i = 1, \dots, m \quad (6)$$

Finally, by obtaining factors of S_i^* and S_i^- , for TOPSIS decision making method a factor of C_i^* can be defined as (Nazari 2018):

$$C_i^* = \frac{S_i^-}{S_i^* + S_i^-} \quad (7)$$

Which the maximum C_i^* presents the best option based on TOPSIS method (Nazari et al 2018).

5. Results and Discussion

In order to evaluate the criteria, ten experts, including seven university professors and three PhD students from University of Tehran and Sharif University of technology, Iran, were surveyed. The experts were chosen based on being familiar with PEC-based hydrogen production and having experience in working with TiO_2 , WO_3 and $BiVO_4$. Eighty percent of respondents participated in this survey have more than two years' experience in the PEC field and half of them has more than five years' experience in this field.

Table 1 shows the normalized criteria scores, resulted from the rating that experts have given to each criterion. The raw scores which are inserted in the score sheets have been in a range of 1 to 7 evaluating each criterion importance from the least important to the most important. The normalized vector shown in Table 1 are based on dividing each criterion raw score to the linear average of all criteria scores.

Table 1. Normalized criteria scores

Criteria	Normalized vector
Study Cost	0.123518
Synthesis Simplicity	0.121542
Facility & Availability	0.11166
Deposition capability on TCO	0.082016
Modifiability	0.123518
Commercialization in H2	
Production	0.143281
Physical and Chemical Durability	0.153162
Eco-friendly Fabrication	0.141304

Based on the results of Table 1, experts believe that physical & chemical durability is the most important factor to be considered for a semiconductor when utilizing in PEC technologies. Commercialization potential and environmental issues are scored as the second and third most important criteria in this material evaluation study.

Experts had also asked to attribute a score between 1 and 7 for each alternative in regards to each criterion. Therefore, by utilizing the criteria weighted scores (shown

in Table 1) and based on the questionnaires scores for each alternative, the normalized vectors of alternatives are achieved. Table 2 shows the weighted normalized vectors of each alternative based on TOPSIS normalization formula represented in eq. 1

The decision-making procedure is between three semiconductors as three alternatives for utilizing in a PEC-based hydrogen production technology. These semiconductors all are familiar by their photo-active nature and their photocatalytic application is compared with each other. The selection of alternatives is based on the diverse advantage of each one that are explained below.

The first material is titanium dioxide (TiO₂), also known as titanium (IV) oxide, is a semiconductor capable of producing hydrogen gas from water. One of the main hindrances of TiO₂ is that it can only activates by UV light. On the other hand, this semiconductor is known for its stability, it is a natural material and it has a wide range of applications, such as sunscreen and paint (Acar & Dincer, 2016; Mills & Le Hunte, 1997; Yourey, 2014).

The second option is tungsten trioxide (WO₃) or tungsten (VI) oxide, which is applied as a photosensitive semiconductor in water splitting technology. This photo-active material can absorb light in visible range, hence, it has drawn a considerable attention as one of the best photoelectrode candidates (Acar & Dincer, 2016; Mills & Le Hunte, 1997).

Bismuth Vanadate (BiVO₄) is the third alternative that similar to WO₃, has a great potential of visible light absorption. Additionally, its durability and performance stability are remarkable. Other applications of this semiconductor are in fields of water treatment and paint industries (Acar & Dincer, 2016; Mills & Le Hunte, 1997; Venkatesan, Velumani, & Kassiba, 2012).

As it is shown in Table 2, comparing the study cost of three semiconductors, experts have chosen TiO₂ as the best option and WO₃ as the second-best alternative. They also believe that TiO₂ can be deposited on the TCO substrates (e.g. FTO or ITO) in more frequent and simpler methods in comparison with BiVO₄ and WO₃. It means that fabricating a TiO₂ photoelectrode is more feasible than the other two options. TiO₂ has also achieved the highest scores in terms of modifiability and durability, while in these two terms BiVO₄ has even higher scores than WO₃.

On the other hand, in term of simplicity of synthesis and also facility needed for this process, PEC experts believe that WO₃ should be in the first place. WO₃ has also chosen as the material with the eco-friendliest fabrication process among these three alternatives. That is while the TiO₂ has less score than BiVO₄ in this criterion, a result that can be attributed to the materials used in TiO₂ synthesis, such as HF (Liu, Yu, & Jaroniec, 2011).

Table 2.
Normalized and weighted vectors for each alternative

Criteria	Semiconductors		
	TiO ₂	BiVO ₄	WO ₃
Study Cost	0.641407	0.425354	0.638491
Synthesis Simplicity	0.632144	0.410631	0.657097
Facility & Availability	0.653057	0.357706	0.667505
Deposition capability on TCO	0.674573	0.441613	0.591548
Modifiability	0.688369	0.53258	0.492449
Commercialization in H ₂ Production	0.693412	0.459842	0.55473
Physical and Chemical Durability	0.68693	0.521172	0.506465
Eco-friendly Fabrication	0.464125	0.547641	0.696188

The next step is to select the maximum and minimum values in each criterion, (illustrated by v_j^* and v_j^-). v_j^* and v_j^- vectors can indicate that in each criterion which alternatives are the best and the worst option.

By having the maximum and minimum vectors, for each alternative the positive and negative ideal solution (S_j^* and S_j^-) can be calculated, resulting in C_i^* vectors to show the final score of each alternative. Finally, by applying the TOPSIS method equation (eq. 7), the best and the worst alternative can be decided.

Table 3 shows the final decision-making scores for three semiconductor candidates.

Based on the obtained scores, TiO₂ is the best choice to investigate in term of bringing the PEC-based H₂ production technology from the R&D level to its prototype level. By a narrow margin, WO₃ is the second reasonable option and BiVO₄ as the last option among these three semiconductors, is expected to drive the least attention.

However, as a developing semiconductor in PEC technology field, this semi-conductive material is less familiar than two other well-known semiconductors, TiO₂ and WO₃. Therefore, it is understandable that the survey may results in choosing BiVO₄ as the least favourite alternative.

Another considerable aspect about the survey results is the ratio of each alternative score regards to the best alternative in every criterion. As it is shown in Table 4, the scores of some alternatives in some criterion are so close to the maximum that it can be considered almost equal with the chosen alternative. For instance, in case of "study cost" criterion, WO₃ is almost as suitable as TiO₂. On the other hand, the score attributed to the synthesis simplicity and material availability of TiO₂ are so close to that of WO₃ that TiO₂ can be considered in an equal priority with WO₃ in these two criteria.

Table 3.
TOPSIS decision making results for each alternative semiconductor

	Semiconductors		
	TiO ₂	BiVO ₄	WO ₃
S*	0.032971	0.075806	0.04232
S-	0.073207	0.012997	0.064795
Topsis (C*)	0.689475	0.146354	0.604913

Table 4.
Scores ratio to the best score of each criterion

Criteria	Semiconductors		
	TiO ₂	BiVO ₄	WO ₃
Study Cost	1	0.663158	0.995455
Synthesis Simplicity	0.962025	0.624917	1
Facility & Availability	0.978355	0.535885	1
Deposition capability on TCO	1	0.654656	0.876923
Modifiability	1	0.773684	0.715385
Commercialization in H ₂ Production	1	0.663158	0.8
Physical and Chemical Durability	1	0.758698	0.737288
Eco-friendly Fabrication	0.666667	0.786629	1

6. Conclusion

In this study, by utilizing TOPSIS decision making algorithm the most suitable semiconductor for a PEC-based hydrogen generation technology is selected. TiO₂, WO₃ and BiVO₄ are three well-known PEC semiconductors that are selected for comparison based on their diverse advantages. The current Multi Criteria Decision Making (MCDM) study is performed by providing a questionnaire based on eight criteria and three alternatives and ten PEC and hydrogen production experts were asked to fill them. "Study Cost", "Synthesis Simplicity", "Facility & Availability", "Deposition capability on TCO", "Modifiability", "Commercialization in H₂ production", "Physical and Chemical Durability" and "Eco-friendly Fabrication" are the eight criteria that are considered in this evaluation.

As the results show, TiO₂ is selected as the best semiconductor in terms of study cost, TCO deposition capability, modifiability, commercialization and durability. On the other hand, WO₃ as another well-known PEC semiconductor is chosen as the best option in terms of synthesis simplicity, Facility & Availability and eco-friendly fabrication. However, based on the survey, BiVO₄ could not surpass the two other famous semiconductors in any criterion. In conclusion, TiO₂ is selected as the best alternative for energy, money and time investment in order to start a PEC-based hydrogen production project

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