Research article
Eurasian J Bio Chem Sci, 2(Suppl 1): 97-101, 2019

Eurasian Journal of
Biological and Chemical Sciences

Journal homepage: www.dergipark.org.tr/ejbcs

The usage of discarded battery coals as electrodes and improving their hydrogen gas production performances by impregnation with Zr and Ce metal oxides

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Received : 26/07/2019
Accepted : 18/11/2019

Abstract: Hydrogen gas ($H_{2(g)}$) production is one of the major topic of the industry and energy production fields, for the last decades. Especially it is popular with showing high energy density. Among the other industrial methods electrolysis is the cleanest one without any by product emissions. It has been very popular to recovery of the discarded materials (such as batteries) as an environmentally friendly equipments. Here the coal of a used up battery is utilized as an electrode in the electrolysis system in order to produce ($H_{2(g)}$). Then these electrodes were modified with impregnation of Zr and Ce metal oxides. At first, $HNO_{3(aq)}$ and $H_2SO_{4(aq)}$ solutions were compared as electrolytes with plain electrodes and $H_2SO_{4(aq)}$ is defined as the optimum electrolyte medium (maximum $H_{2(g)}$ production densities as 24.10xE^{-5} mL sec^{-1} and 87.22xE^{-5} mL sec^{-1},charge densities as 1137.40xE^{-4} C mm^{-2} and 2976.19xE^{-4} C mm^{-2} and current densities as 45.68xE^{-7} A mm^{-2} and 165.34xE^{-7} A mm^{-2}for 0.10 M $HNO_{3(aq)}$ (pH 1.10) and $H_2SO_{4(aq)}$ (pH 1.70) solutions respectively). Then all of these modified electrodes were utilized to the electrolysis system and compared in the case of $H_{2(g)}$ production yield, charge and current density values. The best performances were obtained from CeO_2 modified electrode (maximum $H_{2\ (g)}$ production density as 125.00xE^{-5} mL sec $^{-1}$, charge density as 4265.24xE^{-4} C mm^{-2} and current density as 236.96xE^{-7} A mm^{-2} in 0.10 M of $H_2SO_{4(aq)}$ electrolyte). All of the experiments were duplicated. Hydrogen is one of the most promising, clean and sustainable energy carrier, that can be produced effectively by the usage of CeO_2 modified battery coal.

Keywords: Energy, Battery coal, Hydrogen gas production, Electrolysis, Cerium.

Atık pil kömürlerinin elektrot olarak kullanılması ve daha sonra Zr ve Ce metal oksitleriyle emprenye edilerek hidrojen gazı üretim performanslarının iyileştirilmesi

Özet: Son yıllarda sektörün ve enerji üretim alanlarının ana konularından biri hidrojen gazı üretimidir. Özellikle yüksek miktarda enerji üretilebilmesi açısından hidrojen, yakıt olarak popülerleşmiştir. Elektroliz, zararlı gaz emisyonu oluşturmadığı için diğer endüstriyel yöntemler arasında en temiz olanıdır. Atılan malzemelerin (pil gibi) çevre dostu bir ekipman olarak geri kazanılması da oldukça rağbet gören başka bir alandır. Burada, kullanılmış bir pilin kömürü çıkartılarak, hidrojen gazı ($H_{2\ (g)}$) üretmek için elektroliz sisteminde bir elektrot olarak kullanılmıştır. Daha sonra bu elektrotlar, Zr ve Ce metal oksitleri ile modifiye edilerek elektroliz performansları karşılaştırılmıştır. İlk başta yalın karbon elektrotlar kullanılarak, 0.10 M $HNO_{3(aq)}$ (pH 1.10) ve 0.10 M $H_2SO_{4(aq)}$ (pH 1.70) çözeltilerinin elektrolit olarak performansları karşılaştırılmıştır. Sonuçta 0.10 M $HNO_{3(aq)}$ ve 0.10 M $H_2SO_{4(aq)}$ çözeltilerinin sırasıyla elde edilen maksimum $H_{2\ (g)}$ üretim yoğunlukları 24.10xE^{-5} mL s $^{-1}$ ve 87.22xE^{-5} mL s^{-1}, yük yoğunlukları 1137.40xE^{-4} C mm^{-2} ve 2976.19xE^{-4} C mm^{-2} ve akım yoğunlukları 45.68xE^{-7} A mm^{-2} ve 165.34 xE^{-7} A mm^{-2} olarak ölçülmüştür. Bu nedenle optimum elektrolit) olarak 0.10 M $H_2SO_{4(aq}$ belirlenmiştir. Karbon elektrotlar Zr ve Ce metal oksitleriyle modifiye edilerek elektroliz sisteminde katot olarak kullanılmıştır. Tüm sonuçlar karşılaştırılarak en iyi performansların CeO_2 modifiye edilmiş elektrottan elde edildiği görülmüştür (maksimum $H_{2\ (g)\ \text{üretim}}$ yoğunluğu 125.00xE^{-5} mL s $^{-1}$, yük yoğunluğu 4265.24xE^{-4} C mm^{-2} ve akım yoğunluğu 236.96xE^{-7} A mm^{-2} 0.10 M $H_2SO_{4(aq)}$ elektrolit ortamında). Tüm ölçümler tekrarlanmıştır. Sonuçlar göstermiştir ki CeO_2 modifiye pil kömürünün elektrot olarak kullanıldığı elektroliz sisteminden hidrojen gazı üretimi verimli bir şekilde gerçekleştirilebilmektedir. Elde edilen veriler sürdürülebilir ve temiz enerji eldesi üzerine yapılabilecek çalışmalar için ileri modifikasyonlar yapılarak geliştirilmeye açıktır.

Anahtar Kelimeler: Enerji, Atık pil kömürü, Hidrojen gazı üretimi, Elektroliz, Seryum

1. Introduction

Sustainable energy development requires innovative affords bearing clean energy solutions in it. An energy production method fails from the protocols that needs to explain itself in terms of biocompatibility and low cost demands. So the priority to achieve an acceptable clean energy production procedure has to include at least no hazardous gas emission. There has been many aspects to produce hydrogen gas ($H_{2 (g)}$) such as coal gasification, oil/naphta reforming, electrolysis (Uğurlu et al. 2006, Sen et al. 2016) methane steam reforming, biomass, biological sources (Sivagurunathan et al. 2016; Mujeebu et al. 2016; Seyitoglu et al 2017). $H_{2 (g)}$ consumption performance of the industries are scened as fertilizers (Eren et al. 2010), petroleum refining processes (Erkarslan et al. 2018), petrochemical (Karaoğlu et al. 2010), fuel cells (Karaoglu and Uğurlu 2011), and chemical industries (Züttel et al. 2004; Lim et al. 2015; Lee et al. 2017, Aslan et al. 2018). In electrolysis process, water molecule is the reactant and it is dissociated into hydrogen (H_2) and oxygen (O_2) by the help of external electricity (Kumar and Humabindu, 2019).

Billions of electrodes and fuel cell types were designed to produce energy from electrolysis and the main point of these studies point to the efficient yield achievement. The presented study stands on the efficient electrode development from discarded alkaline battery coals. Zr and Ce were used as the triggering catalyst metals. Previously they have been used on the electrode modifications as highly active hydrogen evoluating catalysts by Demir et al. (2018), and in recent years, efforts to develop heterogeneous catalysts (Karaoğlu et al., 2012; Dinçer at al., 2016) have been accelerated and there are different types of catalyst utilizations (Karahan et al., 2016; Donmez et al., 2018; Gungor et al., 2018; Kara et al., 2018), photocatalysts (Uğurlu et al., 2006; Karaoğlu et al., 2010; Karaoğlu and Uğurlu, 2010). Finally, Zr and Ce used together to improve the catalytic performance reported by Polliotto et al. (2018).

The electrolyte type is also discussed. A suitable electrolyte is expected to be a tramendous charge carrier and nonpoisonous for the electrodes. Up to now several water electrolysis methods are developed and they can be classified in four types based on their electrolyte, operating conditions, and ionic agents (OH^-, H^+, O^{2-}). Queved as (i) alkaline water electrolysis (Zeng and Zhang, 2010), (ii) solid oxide electrolysis (Ni et al. 2009), (iii) microbial electrolysis cells (Kadier et al. 2016) and (iv) proton exchange membrane using water electrolysis (Foteini et al. 2017). Alkaline electrolysis operates with aqueous solution (KOH/NaOH) as the electrolyte but asbestos diaphragm and nickel electrodes should be used (Kumar et al. 2017). Other types of electrolysis cells based on the transfer of electrons through the external circuit to cathode while the protons are passed through to cathode from the pores of proton conducting membrane (as electrolyte) (Rathinam et al. 2018) Acidic electrolytes have been used as being very conventional electrolytes. The most convinient one is the $H_2SO_{4(aq)}$ (pH 1.70) but also $HNO_{3(aq)}$ (pH 1.10) is used as an alternative solution (Lei et al. 2019).

$H_{2 (g)}$ generation experiments were performed in a lab scale basic electrolysis equipment and $H_{2 (g)}$,charge and current generation densities of each system yields were evaluated. The results indicated that $H_2SO_{4(aq)}$ (pH 1.70) is a better electrolyte than $HNO_{3(aq)}$ (pH 1.10) and CeO_2 modified discarded battery coal electrode (CeO_2/C) showed the best fuel cell performances among plain coal electrode (C) and ZrO_2 modified coal electrode (ZrO_2/C). This study, offers a new sight into "environment for environmet" motto. Every single researcher can produce his own hydrogen gas with low voltage inputs and any harmful chemical release.

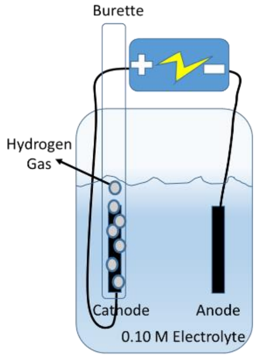
2. Materials and Method

2.1. Materials and chemicals

$H_2SO_{4(aq)}$ (99.80 % pure) (pH 1.70), $HNO_{3 (aq)}$ (99.80 % pure) (pH 1.10), ammonium cerium (IV) nitrate (99.00 % pure), zirconium IV butoxide (99.00 % pure), ethanol (99.00 % pure), from Sigma-Aldrich. Dicarded batteries were obtained from a recovery bin in the building.

2.2. Preperation of the solutions and impregnation processes of the electrodes

In order to prepare 0.10 M $H_2SO_{4(aq)}$ (pH 1.70) and $HNO_{3(aq)}$ (pH 1.10) solutions commercially available stock solutions were used. Required amounts of acids were diluted with deionized water and filled into the electrolysis cell. This solution is sucked into the burette that contains cathode electrode and the volume of hydrogen collected at the top of the burette was measured during the electrolysis was in progress. Scheme is shown below. The coal (C)inside of a discarded AA battery was used as anode or cathode electrode. Modification of the electrodes were achieved by the method as reported by Ghodsi et al. (2011). As it is reported (Ghodsi et al. 2011) the final products are the oxides of these metals. Since the same anions of the metals were achieved on the electrodes synergistic anion effect was prevented for the comparison of the electrode performances. CeO_2/C electrode was prepared as follows: precursor solution was prepared by dissolving $Ce(NO_3)_6(NH_4)_2$ in 10 mL of ethanol and 5 mL of distilled water mixture. Bare C was sucked into this solution completely then stirred for 30 min. Subsequently calcinated for 5 hours at 500 C. Similarly ZrO_2/C was prepared by using zirconium IV butoxide precursor. Obtained electrodes utilized as cathode and C was used as anode for all experiments.



Scheme 1. Electrolysis set up. Anode is C electrode, cathode is adjusted according to the experiment as C, CeO_2/C or ZrO_2/C.

2.3. Electrolysis experiments

Electrolysis experiments were conducted with a beaker and burette at room conditions. Cathode electrode was stucked into the mouth of a 25 mL burette and electrolyte solution was sucked with a bulb into the burette. Anode was maintained as C for all experiments. Firstly dissociation potential measurements were recorded for all electrolysis experiments. After the minimum current was observed $H_{2(g)}$ volume was recorded by running chronometer. Firstly $H_2SO_{4(aq)}$ (pH 1.70) and $HNO_{3(aq)}$ (pH 1.10) electrolytes were compared to each others with C electrodes, then modified electrodes were conducted as cathodes to the 0.10 M $H_2SO_{4(aq)}$ (pH 1.70) filled cell. All of the results are given in the following section.

3. Results

3.1. Calculation of the total $H_{2(g)}$ produced by the systems, charge and current density values

In a typical electrolysis system the volume of the gases have to be determined in order to calculate the amount of charge, current and flow density values. Here the amount of the $H_{2(g)}$ was measured as mL for each experiment set up individually. Then these values were used to calculate $H_{2(g)}$ volume density by dividing into the cathode surface area (439.60 mm^2). Then readed volume of the $H_{2(g)}$ was divided into the theoretical charge of the $H_{2(g)}$ mL 0.12 then charge of the system was obtained. This data was used to calculate current of the system by dividing charge value into the time (second). Current and charge densities were calculated by division of these charge and current values into electrode surface area.

3.2. Comparison of the cell performances of $HNO_{3(aq)}$ and $H_2SO_{4(aq)}$ as electrolytes

At the beginning of the experiments two types of electrolytes were determined as model. Cell performances of the chosen electrolytes were examined with C cathode and anode electrodes. $HNO_{3(aq)}$ (pH 1.10) and $H_2SO_{4(aq)}$ (pH 1.70) were compared to each other in terms of dissociation potential, $H_{2(g)}$ production (Fig.1a), current density (Fig.1b) and charge density (Fig. 1c) performances. An ideal electrolyte is expected to be an excellent charge carrier and has to lead the charge transfer duty well. $H_2SO_{4(aq)}$ is very commonly used electrolyte but $HNO_{3(aq)}$ is also a promising candidate with the high acidic constant near to the $H_2SO_{4(aq)}$. Results of the experiments showed that the dissociation potential value of the $HNO_{3(aq)}$ was measured as 3.60 V whereas $H_2SO_{4(aq)}$ has 3.20 V. This shows that cell potential of the $H_2SO_{4(aq)}$ used electrolysis system is able to run easier than $HNO_{3(aq)}$ in the presence of C electrodes. Additionally $H_{2(g)}$ production, current and charge density values of $H_2SO_{4(aq)}$ are higher than $HNO_{3(aq)}$. As result $H_2SO_{4(aq)}$ was choosen as the electrolyte for subsequent experiments. Table 1 shows the comparison of the cell performance values including modified electrodes at the upcoming sections. This graphs also show that the measured cell performances of the $H_2SO_{4(aq)}$ electrolyte is better than $HNO_{3(aq)}$.

Table 1. Comparison of the dissociation potential, $H_{2(g)}$ production, current and charge density values of the different electrolysis cells.

Cell type	DP*	$H_{2(g)}$ PD**	CD§	CD£
C cathode/C anode in 0.10 M of $H_2SO_{4(aq)}$	3.2	87.22 xE^{-5}	2976.19 xE^{-4}	165.34 xE^{-7}
C cathode/C anode in 0.10 M of $HNO_{3(aq)}$	3.6	24.10 xE^{-5}	1137.40 xE^{-4}	45.68x E^{-7}
ZrO_2/C cathode/C anode in 0.10 M of$H_2SO_{4(aq)}$	2.8	94.44 xE^{-5}	3222.63 xE^{-4}	179.03 xE^{-7}
CeO_2/C cathode/C anode in 0.10M of $H_2SO_{4(aq)}$	2.3	125.0 xE^{-5}	4265.24 xE^{-4}	236.96 xE^{-7}

* Dissociation potential (V); ** $H_{2\,(g)}$ production density (mL sec -1); § Charge density (C mm -2); £ Current density (A mm -2)

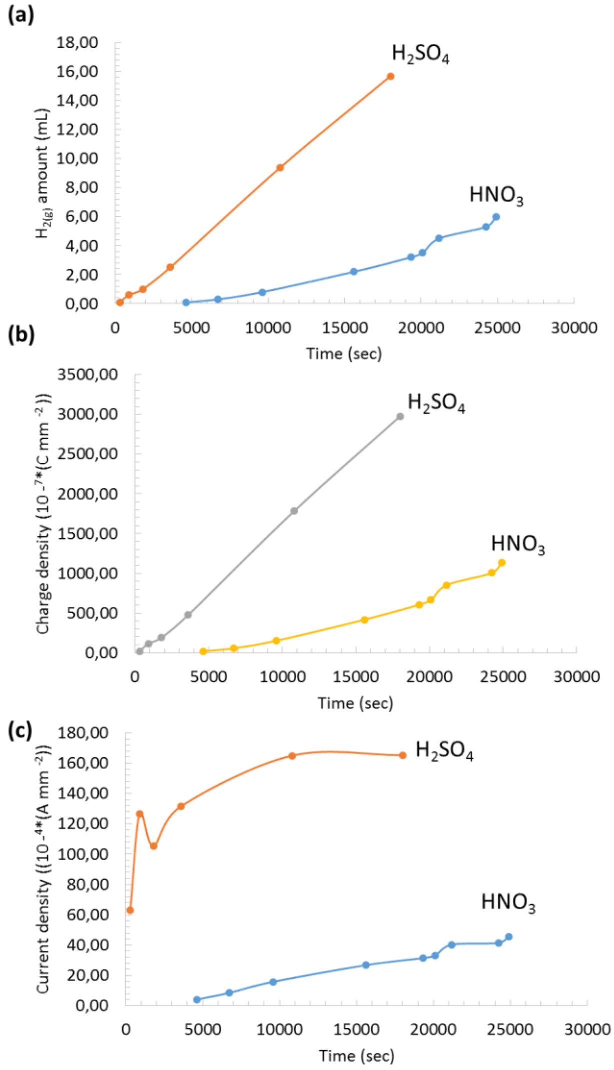


Figure 1. Comparison of the cell performances of two different electrolytes. **a)** $H_{2(g)}$ production performances, **b)** current density curves, **c)** charge density graphics of the 0.10 M $H_2SO_{4(aq)}$ (pH 1.70) and $HNO_{3(aq)}$ (pH 1.10) electrolytes recpectively. All of the measurements were recorded with plain carbon electrodes as anode and cathode, at 21 °C, atmospheric pressure and electrolyte solutions were prepared with distilled water.

3.3. Comparison of the cell performances of C, ZrO_2/C and CeO_2/C cathodes

All of the electrolysis experiments were carried out in 0.10 M of $H_2SO_{4(aq)}$ (pH 1.70) electrolyte at room conditions. After the modification of electrodes they were utilized as cathodes where C electrode was anode. First of all dissociation voltages of the electrodes were compared. As the datas revealed that CeO_2 modified electrode showed the lowest dissociation voltage that means the electrolysis process initiates the easiest by using CeO_2/C electrode among all. That explains the charge transfer efficiency is trigerred by the Ce ions on C electrode. Also the other parameters are supporting this idea as being at maximum levels for CeO_2/C electrode. All of the maximum density values presented after 300 sec. measurement for all of the cathode types. Figure 2 shows the comparison of the $H_{2\,(g)}$ production, current and charge density value plots of the C, ZrO_2/C and CeO_2/C cathodes vs. C anodes 0.10 M of $H_2SO_{4(aq)}$ (pH 1.70) electrolyte containing electrolysis cells.

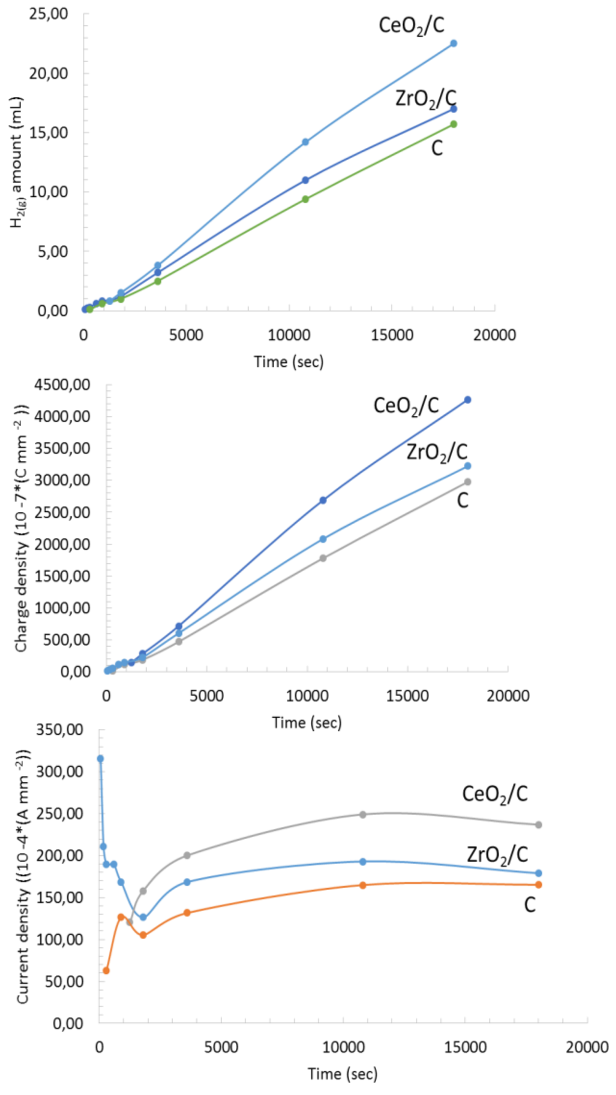


Figure 2. $H_{2\,(g)}$ production, current and charge density value plots of the C, ZrO_2/C and CeO_2/C cathodes vs. C anodes 0.10 M of $H_2SO_{4(aq)}$ (pH 1.70) electrolyte containing electrolysis cells.

3.4. Evaluation of the electrolysis performance of electrodes

This results exhibits the higher $H_{2\,(g)}$ production volumes and cell performances can be achieved by the electrode modification such as CeO_2 and the group elements. Priority of the fuel cells generation of the high energy outputs but if the point is generation and the storage of the $H_{2\,(g)}$ production performance of the cathode comes forward. It pushes the researcher to find new ways to modify electrode so with these current and charge density values system exhibits promising power outputs. Untill now different types of the cells were reported in their specialized measurement parameters but it is clear that solid oxide cells are gaining huge attention (Ni et al. 2009). Proton exchange membrane (PEM) of an electrolysis cell is our next step and these electrodes will be adapted to the PEM body and measurements will be conducted as well.

4. Conclusions

Waste management of the batteries “in terms of coals” recovery and development of these wastes are discussed here successfully. This is a good attempt to obtain energy from wastes in a lab scale set up. Production yields of the electrodes can be improved by the choice of the suitable electrolyte, may the alkaline medium can be preferred also more useful cell type can be selected as solid or PEM electrodes can be used in the future experiments. Hydrogen storage experiments are also upcoming subject of this research.

Acknowledgements

Prof.Dr. M. Hamdi KARAOGLU is greatly acknowledged for their very valuable scientific mentorship.

“This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors”

Conflict of interest disclosure:

There is no conflict of interest.

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