



## Study of some construction parameters on the Air electrode performance of Zinc-Air semi fuel cell

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### Abstract:

In this study effect of construction parameters such as KOH amount, pressure and pressing duration on efficiency of gas diffusion electrode (GDE) in Zinc-Air semi fuel cell (ZAsFC) was investigated. For this propose Linear Sweep Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS) were used for comparing electrodes that constructed with different conditions. The results revealed that the pressure has important role on oxygen reduction and evolution reaction. In optimized condition exchange current for oxygen reduction and evolution were improved for 4 and 10 times respectively.

**Keywords:** Oxygen reduction/evolution reactions, gas diffusion electrode, Zn-air semi fuel cell.

### Introduction:

The oxygen reduction reaction (ORR) occurring at the cathode plays a key role in metal-air batteries [1, 2]. ORR in aqueous solutions occurs mainly by two pathways: the direct 4-electron reduction pathway from O<sub>2</sub> to H<sub>2</sub>O, and the 2-electron reduction pathway from O<sub>2</sub> to hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). In non-aqueous aprotic solvents and/or in alkaline solutions, the 1-electron reduction pathway from O<sub>2</sub> to superoxide (O<sub>2</sub><sup>-</sup>) can also occur [4].

Zn-air semi fuel cell have many advantages including high specific energy, competitive cost, abundant resources, and environmentally benign property, it is expected to be a promising power source and energy storage device in the near future [5]. It is an electro-chemical system powered by the reaction of zinc with oxygen from the air in a basic electrolyte[6]. The key problem the development of Zn-air semi fuel cell is the oxygen-diffusion electrode.

At this study, effect of some construction parameter such as pressing pressure and duration, amount of KOH and pressing frame were investigated.



## Material and methods:

Preparation of gas-diffusion electrodes:

A gas-diffusion electrode is composed of a gas-supplying layer and a catalyst layer with a stainless steel mesh. The gas supplying layer is composed of 10% (W/W) polytetrafluoroethylene (PTFE), 7% (W/W) CMC, 60% (W/W) graphite and 5% (W/W) MnO<sub>2</sub> that were mixed well by mortar. After mixing different volume of KOH (9 M) was added and mixed well. The produced paste was rolled on steel mesh and pressed with various pressure and duration. Then electrode was dried in 200 °C oven.

**KOH amount:** Effect of KOH amount on electrode response was considered. For this purpose effect of KOH amount in electrode was investigated in three levels of 0.09, 0.06 and 0.03 ml of 9 M KOH. Then LSV test results were considered for each electrode with different KOH amounts. For

**Pressure:** To evaluation of pressure effect on electrode response, the pressure of 30, 40, 50, 60, 70, 80, 90 and 100 Bar were considered. The LSV test results of electrode with different pressure were comprised.

**Pressing duration:** effect of pressing duration was investigated in three levels of 10, 15, 20 and 30 minutes

**Electrochemical testing:**

The electrochemical properties of as prepared electrodes were studied by Linear Sweep Voltammetry (LSV) method and Electrochemical Impedance Spectroscopy (EIS) with a three electrode system contain a Ag/AgCl electrode as the reference electrode, a Pt electrode as a counter electrode in 9M OH electrolyte at ambient temperature.

## Results:

Figure. 1 shows the LSV of KOH contents on GDE electrode in cathodic (A) and anodic (B) directions. Electrical potential of the LSV test was selected -0.9 to 0 and 0 to 0.5 v for reduction and oxidation, respectively. By increase in potential for reduction, electrical current converged to zero and a peak is seen in - 0.4 v. By potential sweep in anodic direction current is increased too. For investigation of variation of KOH content on LSV current at potential of -0.8 and 0.3v was selected. The results show that the anodic and cathodic current of electrode with KOH amount of 0.03 ml has the maximum values.

For more investigation tafel analysis was performed by polarizing  $\pm 250$  mV based on open circuit potential to get exchange current. As it is depicted in Table 1 the KOH amount of 0.03 ml is the optimized value.

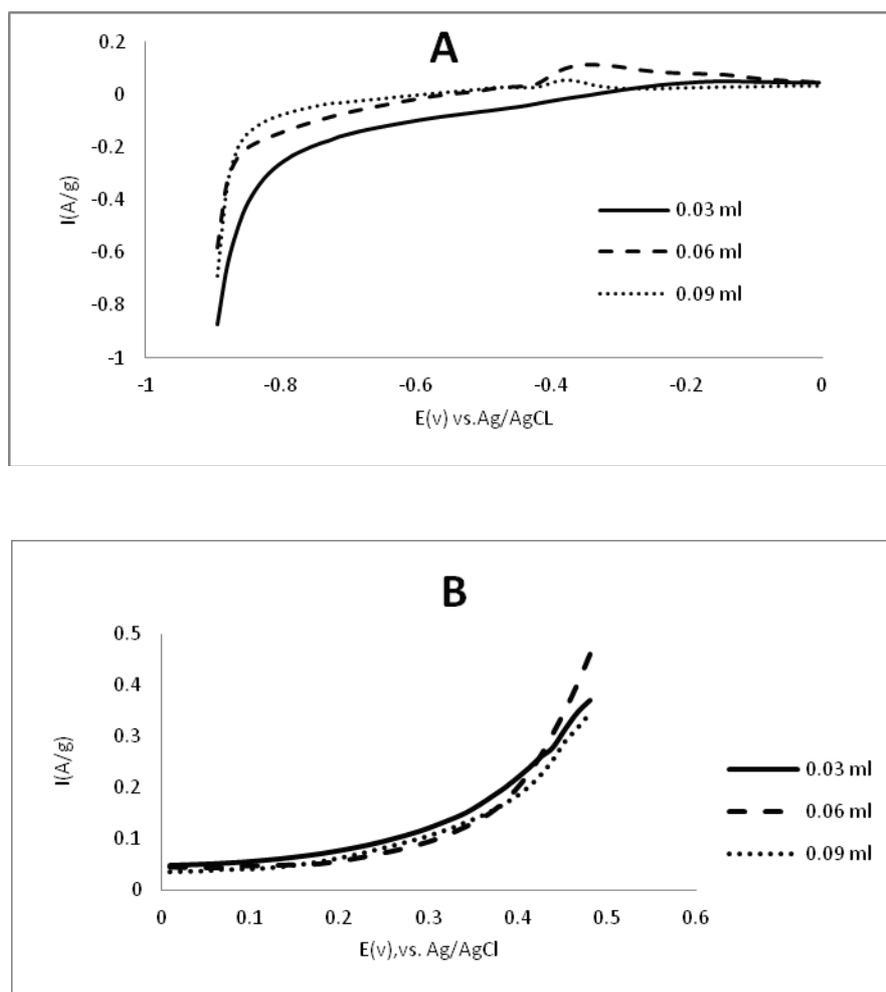


Figure 1: Effect of KOH amount on GDE preparation (A) cathodic direction (B) anodic direction in 9M KOH at scan rate 1 mV/s

Table 1: Effect of KOH content on anodic and cathodic exchange current of GDE

KOH content	$I_{0C}$ mA/g	$I_{0a}$ mA/g	Ocv
0.03 mL	44	27	-0.339
0.06 ml	13.4	4.3	-0.436
0.09 ml	29	36	-0.339

Effect of pressure on GDE was investigated (Figure. 2). Electrical potential of the LSV test was selected -0.9 to 0 volt and 0 to 0.5 volt for reduction and oxidation, respectively. By increase in potential for reduction, current converged to zero and a peak is seen in - 0.4 volt, Figure. 2 A. By increase in potential in oxidation current is increased too, Figure. 2 B.

As it is depicted in table 2, the electrode made under 50 Bar is the best one but the difference between current of electrode prepared under different pressure is low. Optimization criteria

were reduction current at potential of -0.8v was selected also current at 0.3v was selected for oxidation optimization. The LSV curve of electrode (Figure 2) made under 50 bar show that the anode and cathode current of electrode made under is the highest

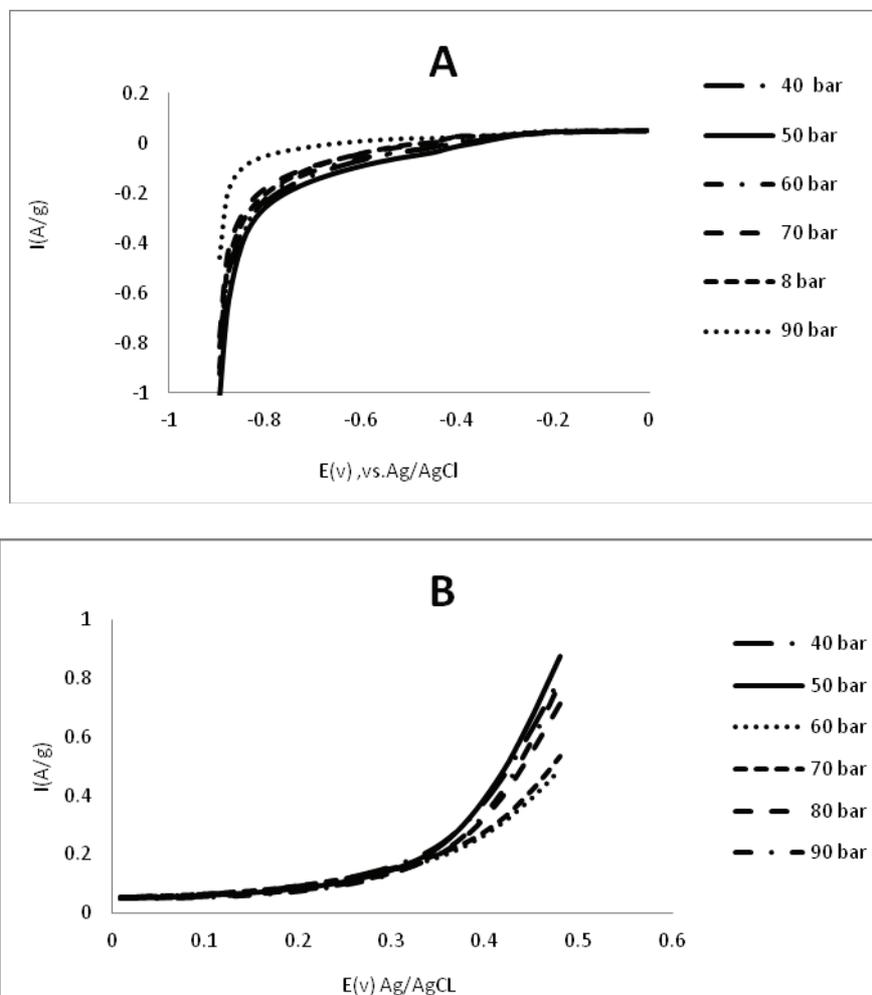


Figure 2: Effect of pressure on GDE preparation (A) cathodic direction (B) anodic direction in 9M KOH at scan rate 1 mV/s

The effect of pressing duration on the performance of GDE is shown in Figure.3. The pressing duration in electrode construction was investigated in different duration time. As it is represented in Table 3 the pressing duration of 15 minute is the optimized value. As mentioned before voltamograms was performed in anodic and cathodic direction for evaluation of pressing duration. By increase in potential for reduction, current converged to zero and a peak is seen in - 0.4 volt. By increase in potential in oxidation current is increased too. For optimization reduction current at potential of -0.8v was selected also current at 0.3v was selected for oxidation optimization. For optimization reduction current at potential of - 0.8v was selected also current at 0.3v was selected for oxidation optimization.

Table 2: Effect of pressure on anodic and cathodic exchange current of GDE.

	$I_{0C}$ mA/g	$I_{0a}$ mA/g	ocv
90 bar	10.7	15.3	-0.644
80 bar	19.5	21.6	-0.45
70 bar	22.1	42.3	-0.464
60 bar	26.4	14.2	-0.408
50 bar	40.7	55.1	-0.352
40 bar	9.3	0.28	-0.422

The LSV curve of electrode (Figure 3) made by pressing duration show that the anode and cathode current of electrode made with the pressing duration is the highest

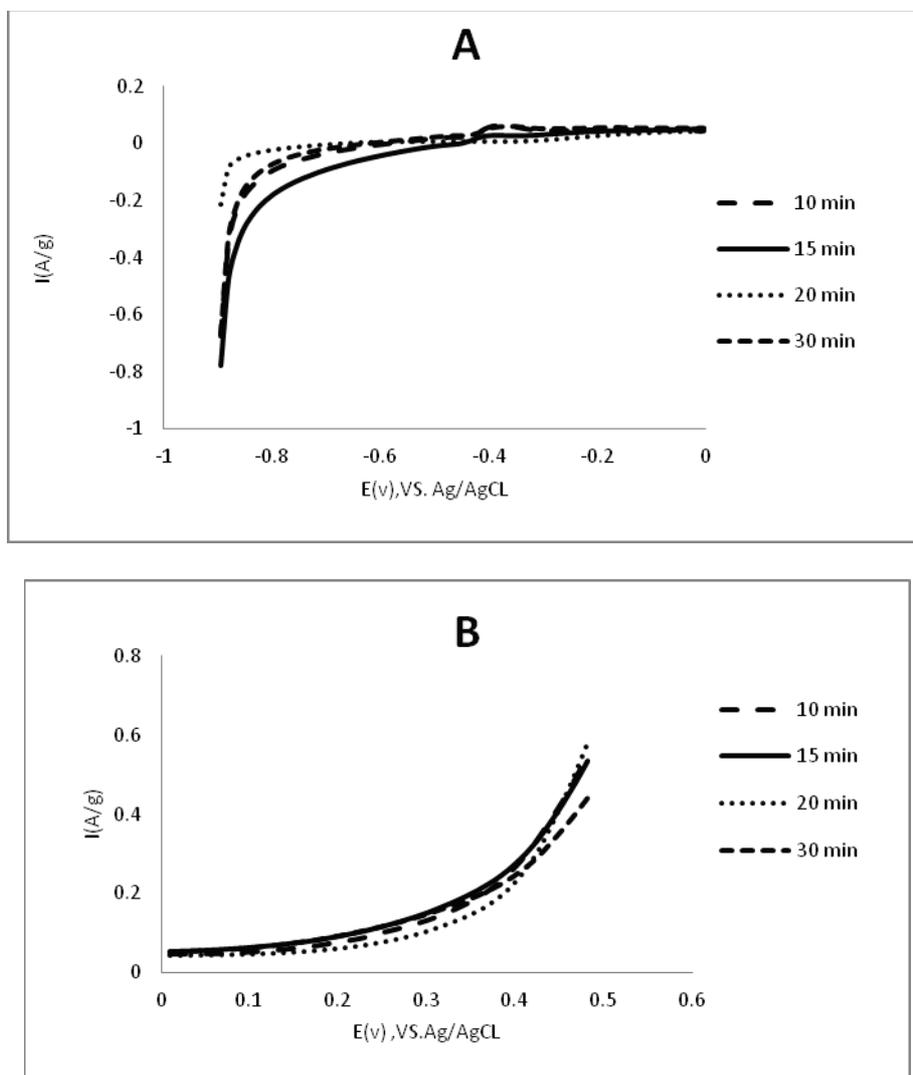


Figure 3: Effect of pressing duration on GDE preparation (A) cathodic direction (B) anodic direction in 9M KOH at scan rate 1 mV/s

Table 3: Effect of pressure duration on anodic and cathodic exchange current of GDE.

pressure duration (min)	$I_{0C}$ mA/g	$I_{0a}$ mA/g	Ocv
10	10.9	11.1	-0.589
15	22.1	42.3	-0.464
20	6.4	5.0	-0.627
30	8.7	10.9	-0.616

The effect of optimization on assembled GDE was investigated further using electrochemical impedance spectroscopy (EIS), with complex impedance plots as shown in Figure.4. The intercept with the real axis at high frequency corresponds to the solution resistance  $R_s$ , a result of the combination of electrolyte ionic resistance, the intrinsic resistance of the active materials and binder in the electrodes, contact resistances of the electrodes to current collectors and contacts of the test cells to instrumentation. Moving to lower frequencies, a depressed semi-circle was observed in all cases, assigned to charge transfer processes occurring at the electrode-electrolyte interface; the diameter of this semi-circle gives an indication of the interfacial charge transfer resistance. This was followed at lower frequencies by a curve tending from 45 to 90° at the characteristic “knee” frequency, indicative of a semi-infinite Warburg component with capacitive behavior as a result of electrolyte diffusion within the electrode pores. The results show that charge transfer resistance after optimization reduced also  $R_s$  of optimized GDE is lower than that before optimized condition.

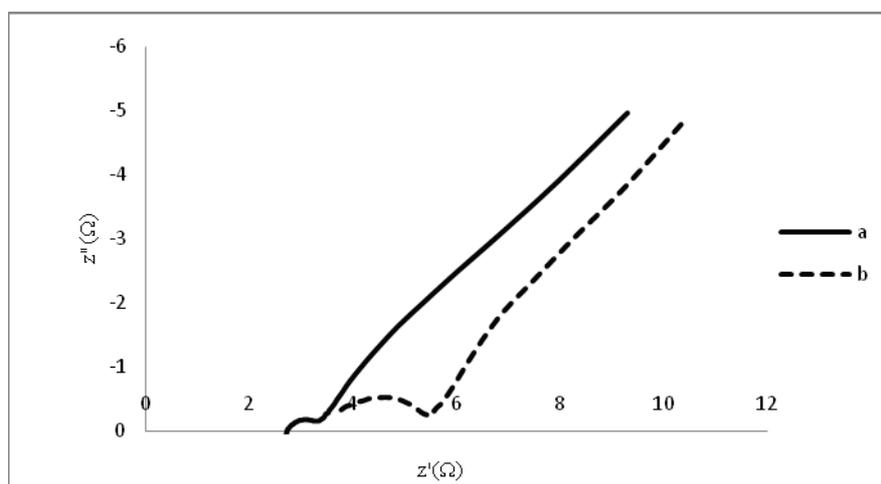


Figure 4: EIS of GDE (a) before and (b) after optimization in 9 M KOH at OCV

Finally the optimized electrode prepared by 0.03 ml KOH (9M), 50 bar pressure and pressure duration 15 min compared with non optimization GDE. It was shown that the optimized electrode has higher performance than non optimized one. The LSV of electrode (Figure 5) shows that the anode and cathode current of electrode before and after of optimization.

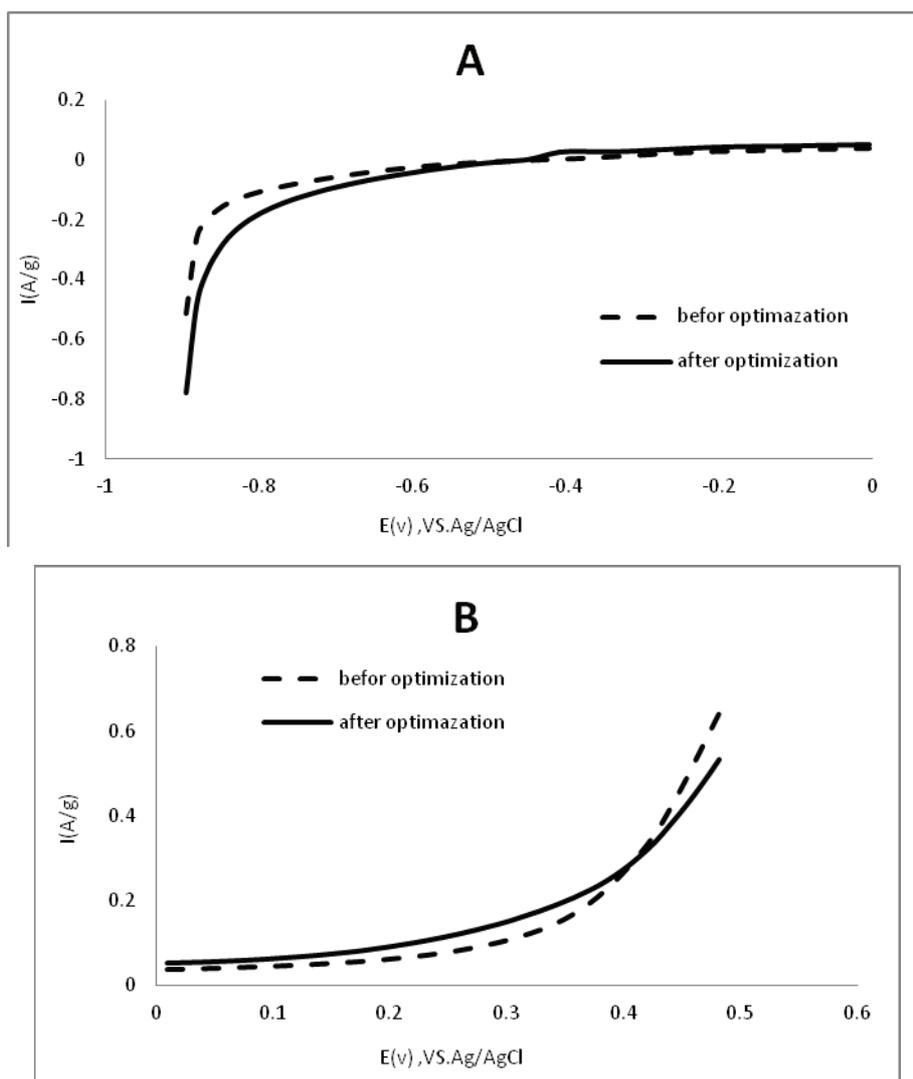


Figure 5: LSV of GDE (A) cathodic direction (B) anodic direction before and after optimization in 9 M KOH at scan rate 1 mV/s

The LSV experiment results for the GDE before and after optimization are shown in Table 4.  $I_{0c}$  after optimization improved around 4 times and  $I_{0a}$  more than 10 times.

Table 4: effect of optimization on exchange current of GDE.

	$I_{0c}$ mA/g	$I_{0a}$ mA/g	Ocv
Before optimization	6.4	4	-0.408
After optimization	22.1	42.3	-0.464



## Conclusions;

Effect of construction variable such as KOH content, pressure and pressure duration on GDE performance has been investigated. When we use optimization condition, the gas diffusion electrode has the best output in produced flow and less resistance. Results show that in optimized condition exchange current for oxygen reduction and evolution were improved for 4 and 10 times respectively.

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