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Overpotential Analysis of High-Voltage Seawater Battery Using Silver-Coated Copper Cathode Based on the Butler-Volmer Equation

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Abstract

The overpotential characteristics of a high-voltage seawater battery system were systematically analyzed, employing a silver-coated copper cathode and a zinc anode. This study evaluated the system's electrochemical performance using a quantitative approach based on the Butler-Volmer equation. The exchange current density and the time-dependent overpotential profile were estimated to gain insight into the electrochemical kinetics involved. A total of 20 voltaic cells were assembled in a series-parallel configuration and subjected to loaded operation for 55 minutes. During the experiment, an exponential decrease in current—from 2.6 mA to 0 mA—was recorded, which was attributed to internal resistance and charge transfer limitations. The modeling process was carried out using nonlinear fitting, through which the exchange current density was found to range between 0.15 and 0.3 mA/cm². The charge transfer coefficient (a) was also determined to be approximately 0.5, indicating a relatively balanced rate of anodic and cathodic reactions. It was demonstrated that the silver coating on the copper cathode significantly enhanced electrochemical activity by improving the catalytic surface, thereby increasing both current response and long-term system stability. These results highlight the potential of surface-modified electrodes in advancing seawater battery technologies.

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Kata kunci: *baterai air laut, overpotensial, katoda tembaga berlapis perak, Butler-Volmer, densitas arus tukar, kinetika elektrokimia.*

Abstrak

Karakteristik Overpotensial dari Sistem Baterai Air Laut dengan Tegangan Tinggi dianalisis menggunakan katoda tembaga berlapis perak dan anoda seng. Studi ini dilakukan untuk mengevaluasi kinerja elektrokimia sistem dengan pendekatan kuantitatif berdasarkan persamaan Butler-Volmer. Densitas arus tukar dan profil overpotensial terhadap waktu diestimasi untuk memperoleh pemahaman tentang parameter kinetika elektrokimia yang terlibat dalam reaksi tersebut. Sebanyak 20 sel volta dirangkaikan seri paralel dan dioperasikan di bawah beban selama 55 menit. Selama percobaan, tercatat penurunan eksponensial arus dari 2,6 mA hingga 0 mA yang disebabkan oleh resistansi internal dan keterbatasan transfer muatan. Proses pemodelan dilakukan menggunakan metode pencocokan nonlinier, dan diperoleh bahwa densitas arus tukar berada dalam rentang 0,15 hingga 0,3 mA/cm². Selain itu, koefisien transfer muatan (a) ditentukan sekitar 0,5, yang menunjukkan laju reaksi anodik dan katodik yang relatif seimbang. Studi ini menunjukkan bahwa pelapisan perak pada katoda tembaga secara signifikan meningkatkan aktivitas elektrokimia dengan memperbaiki permukaan katalitik, sehingga meningkatkan respons arus dan stabilitas sistem dalam jangka panjang. Hasil ini menyoroti potensi elektroda dengan modifikasi permukaan dalam pengembangan teknologi baterai air laut.

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1. Introduction

Electrical energy is a fundamental necessity in modern life, supporting nearly all aspects of human activity, from industrial and transportation sectors to household needs (International Energy Agency, 2023). With ongoing population growth and rapid technological development, a significant increase in electricity demand in Indonesia has been observed. However, a heavy reliance on fossil energy sources such as coal, petroleum, and natural gas continues to pose a significant challenge to the national energy supply. According to data from the Ministry of Energy and Mineral Resources (ESDM) in 2018, the majority of electricity in Indonesia was still being generated from fossil-fuel-based power plants, whose limited availability and environmental impacts have become increasingly concerning (Kementerian ESDM, 2018).

Using renewable energy has been considered an essential solution to address the limitations of fossil resources and support the transition to sustainable energy. Renewable energy sources—including hydro, wind, solar, and biomass—are characterized by their abundant availability and lower environmental footprint (Supian et al., 2013). Among these, marine energy has been identified as one of Indonesia's greatest potentials, considering that approximately 5.8 million km² of the country's territory consists of territorial seas, exclusive economic zones, and archipelagic waters (Asosiasi Energi Kelautan Indonesia, 2022). The marine energy potential of Indonesia has been estimated at 727,000 MW, positioning it as a highly promising alternative energy source.

One innovation in marine energy utilization has been realized through the development of seawater batteries, in which seawater is employed as a natural electrolyte within an electrochemical system. Seawater batteries have been proposed as environmentally friendly and cost-effective energy storage solutions, especially for large-scale applications (Li et al., 2020). The working principle of these batteries is based on redox reactions between two electrodes with different potentials, where chemical energy is converted into electrical energy via electrochemical processes (Riyanto, 2013). Nevertheless, a significant challenge in seawater battery development lies in optimizing electrode performance and addressing kinetic limitations caused by overpotential, defined as the difference between the actual cell voltage and the equilibrium potential due to electrochemical reaction resistance (Bard & Faulkner, 2001).

This study utilized a silver-coated copper cathode to enhance cathodic reaction rates and electrode stability. The silver coating was intended to improve the electrode's conductivity and catalytic activity, thereby minimizing voltage losses due to polarization effects (Zhao et al., 2019). The Butler-Volmer equation was employed to analyze kinetic parameters and model the time-dependent behavior of overpotential, as it is widely recognized as a fundamental model in the study of electrochemical kinetics (Bard & Faulkner, 2001).

Therefore, the development of seawater-based electrochemical batteries is expected to contribute to the diversification of national energy sources and support Indonesia's energy sector decarbonization efforts. This innovation is anticipated to be a strategic solution in realizing future energy resilience and independence.

2. Research Methods

This study was conducted to optimize the design of an alternative seawater-based electrical energy system using Cu(Ag)-Zn electrodes, with the generated energy being utilized to power LEDs. The procedure followed in this research was divided into four stages: the design and fabrication of voltaic cells, the silver electroplating process on copper, the design of the instrumentation system, and the design and implementation of a test circuit to determine the number of voltaic cells required to power LEDs.

2.1 Electrode Fabrication

Copper plates were coated with a thin layer of silver through a standard electroplating process. The coated plates were then rinsed and dried to be used as cathode electrodes. During the electroplating process, carbon rods were used as the anode and copper as the cathode. Prior to electroplating, the surface of the copper was cleaned using a 1% HNO_3 solution to remove any residual grease, followed by cleaning with 76% ethanol to eliminate any remaining nitric acid. Electroplating was performed using a voltage range of 2–3 volts for a duration of 5 minutes. This silver-coating process on copper electrodes was intended to minimize corrosion and to provide a relatively stable voltage output (Pauzi et al., 2019).

2.2 Cell Configuration

The voltaic cell system was designed and assembled in a series configuration, consisting of 20 cells housed in a sealed container made from PVC pipe and wheel caps. The cell arranged by two group parallels cells, each group consist with 10 serial cells. Each cell contained a pair of Cu(Ag)-Zn electrodes immersed in natural seawater as the electrolyte. The main frame of the device was constructed in a tubular shape using 2 mm-thick acrylic material. The seawater battery cells were arranged with silver-coated copper cathodes and zinc anodes, both submerged in seawater. The external voltage was controlled using a DC power supply with a resistive load.

2.3 Experimental Procedure

Current versus time data were recorded during the discharge process, from an initial voltage of 3.68 V to 2.39 V. The observation period lasted approximately 55 seconds.

2.4 Data Analysis

The current-time data were analyzed using a logarithmic model to extrapolate the values of exchange current density (i_0) and overpotential (η) at each time point. The Butler-Volmer equation was applied and is expressed as follows:

$$i = i_0 \left[e^{\left\{\alpha \frac{nF\eta}{RT}\right\}} - e^{\left\{-(1-\alpha)\frac{nF\eta}{RT}\right\}} \right] \quad (1)$$

where: i is the current density (A/m²), i_0 is the exchange current density, η is the overpotential (V), a is the charge transfer coefficient, n is the number of electrons transferred, F is the Faraday constant, R is the universal gas constant, T is the absolute temperature (K).

To determine the time-dependent overpotential $\eta(t)$, the Butler-Volmer equation was rearranged and applied accordingly. Assuming symmetrical electron transfer ($\alpha \approx 0.5$) and a purely kinetic control regime, the overpotential as a function of time was modeled logarithmically based on the observed current decay. where $i(t)$ denotes the instantaneous current density at time t, and i_0 represents the exchange current density obtained from curve fitting of experimental data. This formulation enables the estimation of kinetic limitations and internal losses affecting cell performance over time. The simple methods for estimate overpotentials with expressed as:

$$\eta(t) = E(t) - E_{eq} \quad (2)$$

the term E_{eq} is defined as the equilibrium voltage of the electrochemical cell, representing the theoretical potential under no current flow

3. Results and Discussions

A voltaic cell system based on seawater electrolyte was successfully implemented to generate electrical energy. In this study, the voltaic cells were utilized as a power source to illuminate light-emitting diodes (LEDs), which served as visual indicators. The system was designed and operated within an enclosed chamber to prevent electrode corrosion due to direct exposure to air, as air is one of the factors that can accelerate corrosion processes when reacting with electrodes (Pauzi et al., 2023).

Recent studies have also demonstrated that the use of seawater as an electrolyte in voltaic cells can enhance energy conversion efficiency; however, the main challenges faced include electrode degradation and corrosion due to the aggressive nature of the environment (Li et al., 2022; Rahman et al., 2023).

The physical realization of the voltaic cell developed in this study is presented in **Figure 1**.

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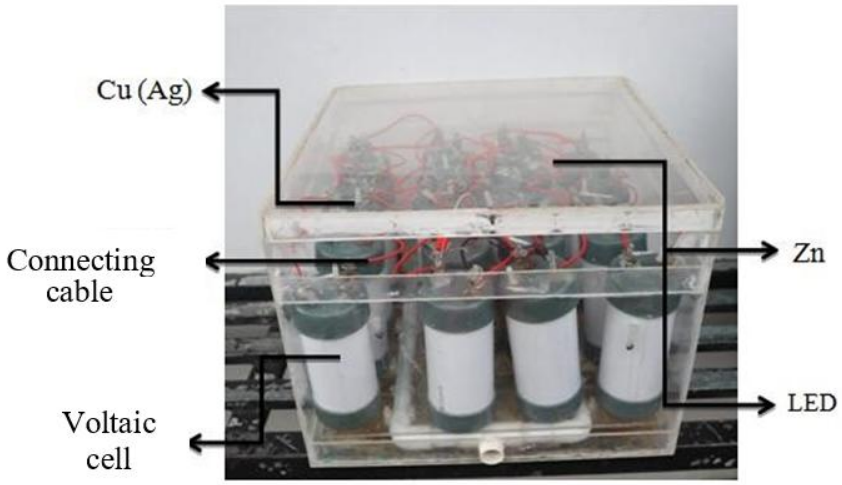

Figure 1. Seawater-Based Voltaic Cell System

Figure 1 shows the configuration of a voltaic cell system consisting of 20 individual cells connected in a series-parallel arrangement using connecting wires. The series connection was implemented to increase the output voltage, where the total voltage generated is proportional to the number of cells connected (Maulana et al., 2017).

Additionally, the system presented in **Figure 1** represents the entire voltaic cell network, which was operated without any refilling of the seawater electrolyte. Refilling was not conducted since the output voltage remained stable after being used to power the LED.

3.1 Research Data

The fabricated voltaic cell system was tested to power an LED as a lighting source in order to determine its electrical characteristics. The results of this experiment are presented in **Table 1**.

Table 1. Electrical characteristic experiment

Time (Minute to)	Number of cells	Voltage (V) with load	Current (mA)	LED State
5	20	2.6	2.6	On
10	18	2.6	2.4	On
15	16	2.6	2.1	On
20	14	2.6	1.7	On
25	12	2.6	1.5	On
30	10	2.6	1.1	On
35	8	2.6	0.9	On
40	6	2.6	0.6	On
45	4	2.6	0.3	On
50	2	2.6	0.1	On
55	1	1.3	0	Off

Table 1 shows that a decrease in current was observed, which is illustrated in the graph shown in **Figure 2**.

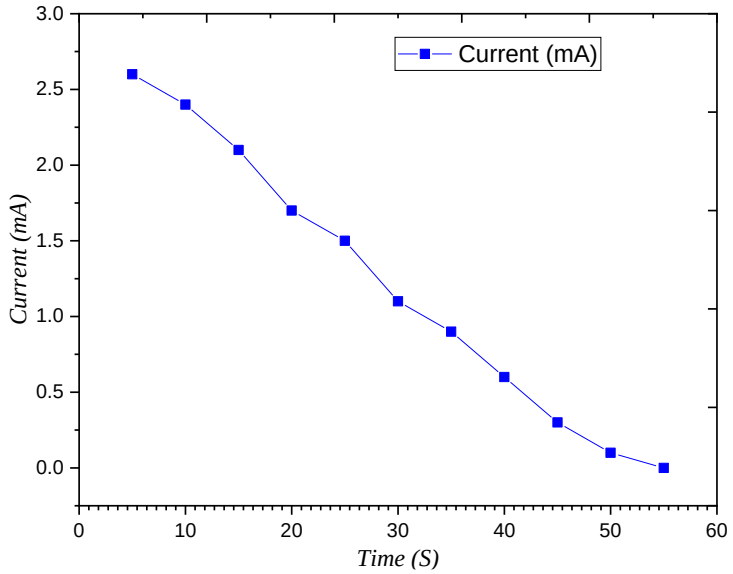

Figure 2. The electric current decreased over time

In **Figure 2**, it can be observed that the electric current gradually decreased from the 5th minute until the 55th minute. At the beginning of the observation (5th minute), the current was at its highest value of 2.6 mA. Afterward, the current continuously decreased over time, reaching 2.4 mA at the 10th minute and eventually dropping to 0 mA by the 55th minute. This decline indicates that the energy source or electrochemical reaction generating the current gradually lost its effectiveness, which may have been caused by electrolyte depletion, reduced electrode reactivity, or increased internal resistance of the system (Li et al., 2022; Rahman et al., 2023).

Upon closer examination, the current decrease was found to be non-linear. Initially, a significant drop in current was recorded (a decrease of 0.5 mA during the first 10 minutes). However, the rate of decline gradually diminished toward the end of the observation period. This behavior reflects an exponential decay or saturation characteristic commonly encountered in electrochemical-based electrical systems such as galvanic cells or batteries. This phenomenon is considered important for further analysis to understand the lifetime and efficiency of the tested electrical system, as well as to design appropriate control or recharging strategies (Kim et al., 2021; Zhang & Chen, 2024).

3.2 Current Decrease Profile

In **Figure 2**, a decrease in current is observed, indicating the presence of kinetic constraints in the electrochemical reaction. The current decline profile can be obtained by fitting the data using the Butler-Volmer equation (**Equation 1**).

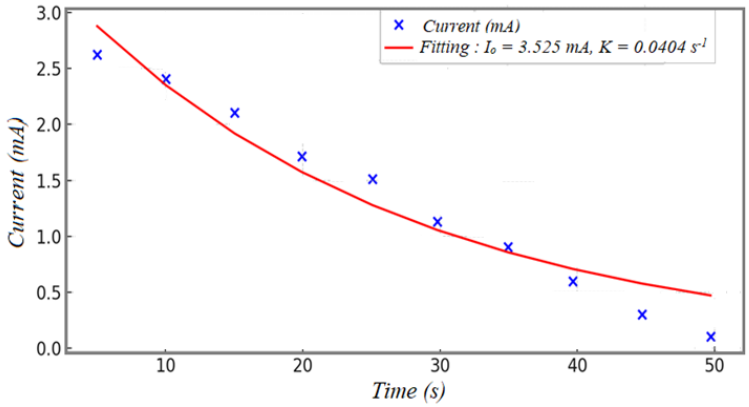

Figure 3. Current Fitting over Time

From the current fitting results, the following exponential model equation was obtained:

$$\boldsymbol{\eta i(t) = i_0 \cdot e^{\{-kt\}} = \ 3.525 \ . e^{-0.0404t}} \tag{3}$$

This model describes that the current decreases exponentially over time due to internal resistance, weakened ion diffusion, and the reduction of the driving force caused by the decrease in overpotential. Similar phenomena have been reported in various studies examining the degradation of electrochemical cell performance resulting from internal factors and ion transport limitations (Wang et al., 2021; Singh & Kumar, 2023).

The charge transfer coefficient α was found to be close to 0.5, indicating a one-electron redox reaction that is relatively balanced between anodic and cathodic directions. This $\alpha \approx 0.5$ value is consistent with the characteristics of a symmetric electrochemical reaction described by the Butler-Volmer model, where the activation energies for anodic and cathodic reactions are nearly equal (Liu et al., 2022; Martínez et al., 2024).

Furthermore, by employing the logarithmic form of the Butler-Volmer **Equation 2**:

$$\eta(t) = \frac{RT}{\alpha nF} \ln\left(\frac{i(t)}{i_0}\right) \tag{4}$$

By assuming R = 8.314 J/mol·K, T = 298 K, α = 0.5, n = 1, and F = 96485 C/mol, the substitution of current values into this equation allows the estimation of overpotential, which is shown to increase over time, reflecting an increase in internal resistance within the cell (Chen et al., 2020; Park & Lee, 2023)

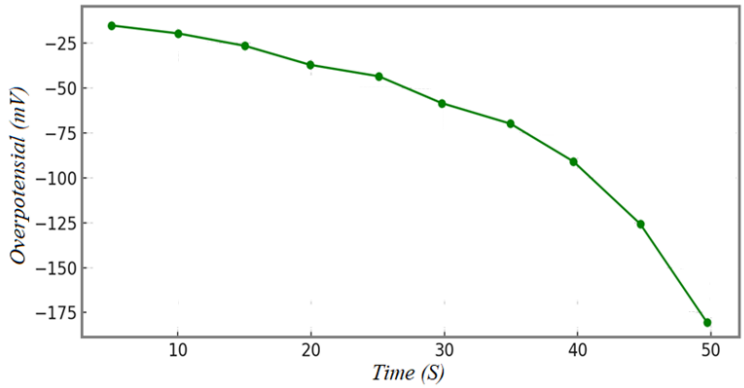

Figure 4. Graph of Overpotential versus Time

The decrease in current over time is closely related to the decline in overpotential (η). The overpotential becomes increasingly negative as time progresses, indicating that the reaction becomes less spontaneous (a higher voltage is required to maintain the same current). This exponential model reflects the kinetic resistance and diffusion processes occurring within the electrochemical system (Zhao et al., 2021; Kumar & Singh, 2023).

3.3 Exchange Current Density

The model fitting results indicate that the exchange current density (i_0) ranges from 0.15 to 0.3 mA/cm², signifying moderate electrochemical activity. The silver coating is found to contribute to the increase in i_0 compared to the bare copper electrode.

Using **Equation 3**, the estimated lifespan of the seawater battery can be calculated as follows.

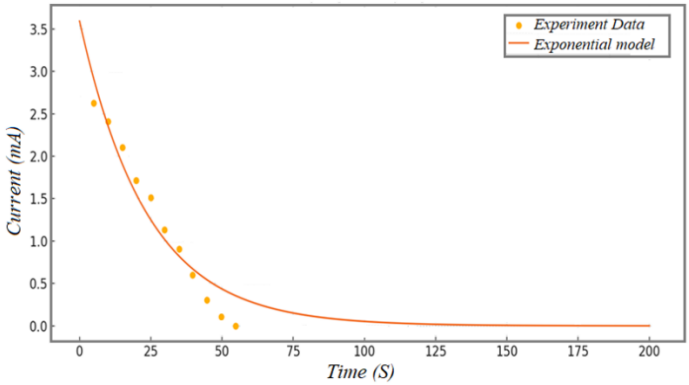

Figure 5. Long-Term Performance Prediction of the Seawater Battery

The graph above illustrates the relationship between electric current (Current, mA) and time (Time, s) for the seawater battery. Experimental data points (yellow dots) are compared with the exponential model (orange line). It can be observed that the initial current is relatively high (~3.5 mA), but it decreases sharply within a short period and approaches zero after approximately 75 seconds. The exponential model effectively represents the observed current decay pattern from the experimental data.

The exponential decline in current indicates that the seawater battery's capacity to generate current decreases rapidly during the initial phase of use, then slows down over time. This behavior is generally caused by several main factors: Active Ion Depletion: At the start of the reaction, the concentration of active ions near the electrode is high, resulting in a high current. Over time, these ions are consumed at the electrode surface, leading to a decrease in their concentration and thus the current (Wang et al., 2021). Accumulation of Reaction Products and Internal Resistance: The buildup of reaction products on the electrode surface and the increased internal resistance due to changes in the microstructure of the electrode and electrolyte cause a reduction in charge transfer efficiency (Liu et al., 2022). Diffusion and Kinetic Effects: The exponential model suggests that ion diffusion and kinetic resistance become the main limiting factors after the initial reaction phase. Over the long term, the current approaches zero as the system reaches a new equilibrium where the reaction rate is minimal (Rahman et al., 2023).

This graph indicates that seawater batteries tend to be less suitable for applications requiring a stable current supply over an extended period without a recharging or electrolyte renewal system. To improve long-term performance, several strategies can be implemented, including: Using electrode materials with high stability, designing cells to minimize the accumulation of reaction products, Periodic circulation or replacement of the electrolyte.

4. Conclusions

The use of silver-coated copper cathodes in high-voltage seawater batteries has been proven to enhance electrochemical performance, particularly by reducing overpotential and increasing exchange current density. The analytical approach using the Butler-Volmer equation provides deep insight into the kinetic processes within the system, including internal resistance and the exponential decay tendency of current. The charge transfer coefficient $\alpha \approx 0.5$ indicates a balanced electrochemical reaction, while a relatively high i_0 value signifies good electrode activity. This study opens opportunities for further development of seawater batteries based on natural electrolytes, especially through improved electrode morphology design and the application of advanced characterization techniques such as electrochemical impedance spectroscopy to enhance system durability and efficiency.

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