Energy Conversion from Aluminium and Phosphate rich solution via ZnO Activation of Aluminium

G. Slaughter, Joshua Sunday and Brian Stevens

Bioelectronics Laboratory, Department of Computer Science and Electrical Engineering, University of Maryland Baltimore County, Baltimore, MD 21250, United States.

Electrochemical power sources have motivated intense research efforts in the development of alternative ‘green’ power sources for ultra-low powered bioelectronic devices. Biofuel cells employ immobilized enzymes to convert the available chemical energy of organic fuels directly into electricity. However, biofuel cells are limited by short lifetime due to enzyme inactivation and frequent need to incorporate mediators to shuttle electrons to the final electron acceptor. In this context, other electrochemical power sources are necessary in energy conversion and storage device applications. Here we report on the fabrication and characterization of a membrane-free aluminium/phosphate cell based on the activation of aluminium (Al) using ZnO nanocrystal in an Al/phosphate cell as a ‘green’ alternative to the traditional enzymatic biofuel cells. The hybrid cell operates in neutral phosphate buffer solution and physiological saline buffer. The ZnO modifier in the phosphate rich electrolyte activated the pitting of Al resulting in the production of hydrogen, as the reducing agent for the reduction of H_2PO_4^- ions to HPO_3^{2-} ions at a formal potential of -0.250 V vs. Ag/AgCl. Specifically, the fabricated cell operating in phosphate buffer and physiological saline buffer exhibit an open-circuit voltage of 0.810 V and 0.751 V and delivered a maximum power density of 0.225 mW cm⁻² and 1.77 mW cm⁻², respectively. Our results demonstrate the feasibility of generating electricity by activating Al as anodic material in a hybrid cell supplied with phosphate rich electrolyte. Our approach simplifies the construction and operation of the electrochemical power source as a novel “green” alternative to the current anodic substrates used in enzymatic biofuel cells for low power bioelectronics applications.

Keywords: Oxides, nanostructures, sol-gel growth, atomic force microscopy

Correspondence and requests for materials should be addressed to G. Slaughter (gslaughter@umbc.edu)

Introduction

Enzymatic biofuel cells employ enzymes as biocatalyst to achieve electrocatalytic oxidation of organic fuel and reduction of oxygen, thereby converting the chemical energy stored in fuel into bioelectricity via redox reactions [1-6] from complex media. The most common biocatalysts employed in glucose biofuel cells are glucose oxidase, glucose dehydrogenase, laccase and bilirubin oxidase [7-9]. These enzymatic based glucose biofuel cells have been proposed as promising ‘green’ alternative energy source that can sustain the energy demand for bioelectronic devices and small portable electronic devices requiring low power density batteries [8, 10-12]. Although glucose dehydrogenase is the most frequently used enzyme in biofuel cells, it requires the immobilization of NAD⁺ cofactor. The co-immobilization of NAD⁺ cofactor requires the utilization of complex procedure [13], which limits its application in bioelectronic devices [14]. Thus, in order to achieve kinetically preferential electron transfer, O₂ dependent and NAD⁺ dependent enzymatic biofuel cells must employ complex multimolecular arrangement in the fabrication of the cells. These multimolecular ensembles are not readily adaptable for batch fabrication and are insufficient to provide the long-term power that bio-implantable electronic devices require. Moreover, current biofuel cells still rely on the immobilization of biocatalyst on low-cost anodic and cathodic materials that are good electrical conductors, such as carbon nanotubes [15-18] and nanowires [9]. Nevertheless, these enzymatic based biofuel cells are still limited by the short lifetimes of the

enzymes due to the denaturation and desorption of the enzymes. This further leads to the instability of the biofuel cell overtime.

Therefore, the generation of energy via novel non-enzymatic anodic substrates is of great importance because of their potential applications in realizing stable source of energy for powering bioelectronic devices. The use of metallic aluminium (Al) in hybrid cell systems eliminate the need for complex and complicated enzyme immobilization strategy, the limitation presented by enzyme inactivity, and the limited power output in enzymatic based biofuel cell systems. The investigation of the activation of Al in physiological saline buffer is an attractive area in energy conversion applications in order to further improve the performance of electrochemical power sources for ultra-low power implantable bioelectronic devices. Although Al is highly reactive, it is protected by a surface layer of inert transparent Al₂O₃ film (3-6 nm thick) that forms immediately upon exposure to air and/or water, thereby providing excellent corrosion resistance [19-20]. However, Al will react with aqueous alkaline and acidic solutions to generate hydrogen [21-27] and various anions such as, Cl⁻ and gluconate anions have been shown to induce pitting corrosion of Al in water [25-29]. The use of these anions permit the direct reaction of Al and water to generate hydrogen gas under ambient conditions, which can be used in the development of hydrogen fuel cells [30]. Here pitting corrosion is employed to activate Al and employ the product, hydrogen, as a reducer in a hybrid aluminium/phosphate cell system.

Aluminium has been extensively researched as an electrode material because of its geological abundance, strong reducing capability ($E^\circ = -1.662$ V), high specific energy density, low cost, environmentally benign reactions and recyclable aluminium hydroxide byproduct [31-35]. In addition to the above studies using alkaline, acidic or pure water solution for pitting corrosion of Al, there are no reports in the literature using phosphate rich electrolyte in combination with ZnO nanocrystal modifiers to activate Al. In this work we characterize the activation of Al anode using ZnO nanocrystal modifier in phosphate rich electrolyte for aluminium/phosphate cell. This study demonstrates that ZnO nanocrystals could be used as modifiers on Al foil for the production of hydrogen and electricity in the presence of phosphate buffer or physiological saline buffer through a pitting corrosion originating from point defects [36]. Furthermore, we demonstrate that the pitting of Al results in the production of hydrogen that acts as the reducing agent for the reduction of H_2PO_4^- ions to HPO_3^{2-} ions for use in aluminium/phosphate cell.

Results and discussion

Effect of ZnO Modifier

The final ZnO seed layers prepared via sol-gel and dip-coating techniques can be described as films of white nanocrystals on the Al/Au support substrate. To confirm this, atomic force microscopy (AFM) was performed to reveal the surface topography of the thin ZnO layer on Al/Au support and bare Al/Au and to measure their roughness. The AFM images presented in Figure 1A shows the formation of ZnO nanocrystal films that are distributed all over the surface of the electrode, suggesting homogeneously dispersed ZnO nanocrystals on the Al/Au support. In addition, the root mean square (RMS) roughness parameter value for Al/Au was 7.68 nm and 62.2 nm for Al/Au/ZnO. The surface of the Al/Au/ZnO is much rougher than the Al/Au substrate. The annealing of the ZnO resulted in the formation of these networked nanostructure films on the electrode surface. Thereby, nanostructuring the Al with ZnO transforms the relatively smooth Al/Au surface into the fully roughened electrically connected assembly of ZnO. This nanostructured surface allows significantly more Zn^{2+} to be plugged in by the electrode surface and, as a result, leading to significant increase of the Al/Al³⁺ oxidation via pitting mechanism originating from the defect site to overcome the thin oxide film on the Al substrate.

To confirm the formation of pitting corrosion on the Al substrate in phosphate rich electrolyte, experiments with Al without ZnO modifier (bare Al) and with ZnO (Al/Au/ZnO) were carried out. The scanning electron microscopy (SEM) micrographs in Figure 1B shows that the bare Al exhibits a smooth morphology and many mechanical scratches. The bare Al after being in contact with phosphate rich electrolyte does not show any significant sign of corrosion. On the other hand, the ZnO modifier on the Al substrate consist of densely packed nanometer-sized grains with mean grain size of approximately 22 ± 3 nm in diameter. It was observed that the byproduct $\text{Al}(\text{OH})_3$ forms only on the ZnO modified Al substrate during discharging in phosphate electrolyte. This suggest that the uniform hydrothermal growth of ZnO nanocrystal over the surface of Al appear to have worn out the initial passive Al_2O_3 layer and thereby enabling the reaction of hydrogen generation from Al in reaction (1).

It is clear that the oxidation of metallic Al in water is thermodynamically favourable reaction that results in the production of hydrogen and $\text{Al}(\text{OH})_3$ [37]. In contrast, there were no notable changes in the structural morphology of the Al substrate after discharging in phosphate buffer, indicating that the thin Al_2O_3 film on the Al substrate without ZnO modifier provides corrosion protection of the Al surface by preventing oxygen and anion transport to the metal surface, which is consistent with the literature reports^{19-20, 36}. Thereby, the ZnO modifier aides in the corrosion of metallic Al to generate $\text{Al}(\text{OH})_3$ film and hydrogen gas on the surface of the Al anode in phosphate electrolyte. Discharging in phosphate buffer solution causes the formation of smaller $\text{Al}(\text{OH})_3$ grains and promotes a more compact and uniform coating, which may further lead to better corrosion protection. Another observation is that there was a noticeable change in the microstructure of the $\text{Al}(\text{OH})_3$ formed in physiological saline buffer. It exhibited blocks of standing flakes surrounded by particles. This suggests that the presence of Cl^- ions in the physiological saline buffer can readily transport through the oxide film during pitting corrosion [38] and the $\text{H}_2\text{PO}_4^-/\text{HPO}_3^{2-}$ anions in the buffer solution react with the solid phase surfaces of ZnO nanocrystals by adsorption and precipitation [39]. This further indicates that in the presence of phosphate, reactions such as Zn^{2+} release from ZnO nanocrystals and the adsorption and precipitation of HPO_3^{2-} induced the microstructural transformation of the $\text{Al}(\text{OH})_3$ layer to form $\text{Al}(\text{OH})_3$ and ZnHPO_3 composite. As the discharge time increases, the corrosion below the oxide film at the defect sites grows and new sites start pitting. Subsequently, the pressure created from the evolution of hydrogen causes the already formed $\text{Al}(\text{OH})_3$ and ZnHPO_3 composite to detach from the Al substrate followed by the formation of new Al_2O_3 film on top of the Al. The reaction byproduct, $\text{Al}(\text{OH})_3$ and ZnHPO_3 **amorphous** composite was confirmed by NMR, EDX and XPS.

Characterization of Reaction Byproducts

The chemical structure of $\text{Al}(\text{OH})_3$ and ZnHPO_3 were confirmed by the ^1H NMR and ^{31}P NMR. As can be seen in Figures 2A, only a single peak at 0.72 and 6.1 ppm was found for potassium phosphate buffer and the $\text{Al}(\text{OH})_3$ and ZnHPO_3 composite byproduct in the ^{31}P NMR spectra, respectively. The singlet at 6.1 ppm is attributed to zinc phosphite, which is in agreement with the literature assignment [40]. The ^1H NMR exhibits a singlet and a multiplet centered at 4.7 ppm for proton site associated with phosphates for potassium phosphate and the $\text{Al}(\text{OH})_3$ and ZnHPO_3 composite, respectively. The singlet observed at 4.1 and 5.2 ppm is attributed to the Al-OH proton sites of $\text{Al}(\text{OH})_3$ and the peak at 6.0 is associated with phosphites for ZnHPO_3 . **In addition, similar results were obtained for the electrolyte, with a singlet and a multiplet centered at 4.7 ppm, thereby suggesting the migration or detachment of the amorphous byproduct from the electrode surface into the electrolyte. Moreover, trace amounts of Au were not present in the resulting electrolyte.** These results are consistent with the literature reports [41-45].

X-ray photoelectron spectra (XPS) of the byproduct obtained from the Al/Au/ZnO anode after discharging in physiological saline buffer were collected to confirm the formation of $\text{Al}(\text{OH})_3$ and ZnHPO_3 . The XPS results showed distinct aluminium, zinc, oxygen, and phosphorous peaks (Figure 2B). These results suggest the formation of the protective $\text{Al}(\text{OH})_3$ and ZnHPO_3 composite with $\text{Zn}2p$, $\text{O}1s$, $\text{P}2p$, $\text{Al}2s$ and $\text{Al}2p$ at binding energies 1022.05, 531.90, 131.10, 119.60 and 73.9 eV, respectively, are attributed to the formation of ZnHPO_3 and $\text{Al}(\text{OH})_3$ [46-47]. The $\text{C}1s$ signal signifies the presence of air-borne contamination. Quantitative XPS analysis showed the

Zn/P atomic ratio to be ~0.5, which was not close to the 1.5 expected for zinc phosphate crystals. This lower Zn/P value indicates the film is amorphous.

To reveal the trace elements in the $\text{Al}(\text{OH})_3$ and ZnHPO_3 composite that detach from the Al/Au/ZnO anode surface after discharging, inductively coupled plasma mass spectroscopy (ICP-MS) analysis were carried out for trace Al and Zn element in 10% nitric acid. It was found that Al was the major constituent of the byproduct composite as shown in Figure 2C and this may likely be attributed to the enhanced hydrogen evolution from the corrosion of metallic Al in physiological saline buffer.

Effect of Corrosion of Al anode and the reducing capability of hydrogen

To evaluate the effect of the pitting corrosion of the Al/Au/ZnO anode in aiding the use of hydrogen as a reductant, cyclic voltammetry (CV) was employed to oxidize water in phosphate electrolyte at extremely high potentials to generate oxygen at the bare Al and Al/Au/ZnO anodes. Results of the electrochemical measurements of the currents of the anode are shown in Figure 3A. At high potential, the oxidation of water in air-saturated phosphate buffer resulted in the highest oxidation current density ($5.1 \mu\text{Acm}^{-2}$) and a relatively low cathodic current density of $-0.15 \mu\text{Acm}^{-2}$ in the presence of Al/Au/ZnO. A pair of well-defined redox peaks was observed at ca. 1.7 V and 0.48 V vs. Ag/AgCl for the oxidation of water and reduction of oxygen, respectively. **The Al/Au anode exhibited electrocatalytic activity towards the oxidation of water at high potentials with a current density of $3.66 \mu\text{Acm}^{-2}$ and cathodic current density of $-0.54 \mu\text{Acm}^{-2}$, whereas the Al anode exhibited insignificant electroactivity.** These results reveal that ZnO modifier exhibit electron transfer activity that can enhance the pitting corrosion of the Al. **Thereby, Al anode will use as the base line anode due to its insignificant electroactivity.**

When metallic Al is in contact with water, the mobile species, water molecules (or OH^- ions) react with the Al, resulting in hydrogen evolution [36]. In fact, both hydrogen and metallic Al are possible reductant species in this reaction system. Figure 3B shows the CV of the BuckyPaper in H_2 -saturated environment and the scan reveals that hydrogen is effective in reducing phosphate in the phosphate electrolyte. Previously mentioned above, the H_2PO_4^- can adsorb on the electrodes in the early stages of corrosion and be reduced to HPO_3^{2-} ions that in turn react with the solid phase surfaces of ZnO nanocrystals by adsorption and precipitation. Thus, the hydrogen diffuses to the top of the $\text{Al}(\text{OH})_3$ film and facilitate the reduction of H_2PO_4^- in phosphate electrolyte at a formal potential of -0.250 V vs. Ag/AgCl. This may suggest that this reduction does not acquire the electrons released from the oxidation of Al beneath the non-conductive Al_2O_3 layer, but from the oxidation reaction (2) of hydrogen on the top of the oxide film.

The hydrogen produced as a result of the pitting corrosion of Al cannot reduce the $\text{Al}(\text{OH})_3$ because of its very low standard reduction potential of $E^\circ_{\text{Al}(\text{OH})_3/\text{Al}} = -2.31$ V. Thus, the electrons released from the oxidation reaction on top of the $\text{Al}(\text{OH})_3$ film recombines with the H_2PO_4^- ions on the surface of the cathode to reduce it to HPO_3^{2-} ions. These ions then react with Zn^{2+} release from ZnO nanocrystals and the adsorption and precipitation of HPO_3^{2-} results in the formation of $\text{Al}(\text{OH})_3$ and ZnHPO_3 composite. This composite detach from the Al substrate when the oxide below is

broken and new oxide forms on top of the Al. Hence, the Al activated by pitting corrosion has the reducing capability of hydrogen, which is used to reduce H_2PO_4^- as shown in the following cell reaction (3) [48].

at the cathode to generate HPO_3^{2-} ions. This further suggests that the dissolution of ZnO in phosphate results in the release of OH^- ions by the replacement of the OH^- ions with the reduction product, HPO_3^{2-} ions, to form ZnHPO_3 , leading to the decrease in H^+ concentration in the solution. This increased the pH of the phosphate electrolyte to 8.2 upon discharging in phosphate electrolyte and further lead to the formation of $\text{Al}(\text{OH})_3$ and ZnHPO_3 composite. This reaction is beneficial in connection with corrosion protection of metallic electrodes under physiological condition, where it may reduce the current and extend the life of the anode.

Complete hybrid cell supplied with phosphate rich electrolyte

Results of the potentiostatic polarization curves obtained with the bare Al and Al/Au/ZnO anodes are shown in Figure 4. The bare Al anode show nearly no catalytically activity because the current densities were less than $1 \mu\text{A cm}^{-2}$. This indicates that the Al surfaces is relatively smooth and does not have an electroactive species bound and electrically connected with the electrode. Whereas, the growth of ZnO nanocrystals on the surface of Al/Au greatly enhances the surface roughness of the electrode. All these indicates that the Al/Au electrode modified with ZnO generates greater current density than the bare Al surface because of the electrical connection established between the ZnO and the metallic Al surface.

The performance of the Al/Au/ZnO anode was evaluated with BuckyPaper as the cathodic electrode in a single compartment cell configuration at different external loads (1 k Ω to 1 M Ω) in phosphate buffer and physiological saline buffer in air-saturated environment. This membraneless cell is especially unique with respect to hybrid cells as most operate using a membrane in order to isolate the anode and cathode during cell operation. The generated electrons from the anode flow to the cathode through the external load circuit. **The reaction mechanism**, current density-voltage and power density-current characteristics for phosphate buffer and physiological saline buffer are presented in Figure 5. The observed open circuit voltage and power density of the phosphate buffer cell were 0.810 V and 0.225 mW cm^{-2} at a current density of 1.36 mA cm^{-2} , respectively. These values are lower than the expected and this may be a result of the byproduct absorptivity at the anode, which inhibits the anode performance. Consequently, the maximum power density was increased eightfold to 1.77 mW cm^{-2} at a current density of 11.95 mA cm^{-2} when operating in physiological saline buffer cell. **The higher current density observed in the presence of physiological saline buffer is attributed to the Cl^- ions in physiological saline buffer, which can readily wear out the oxide film and readily access the Al, thereby inducing a greater degree of pitting corrosion of Al. The current-producing reaction continues until no more Al sites are available for pitting, thus no current flow through the system.** Control experiments using bare Al as the anode in phosphate buffer, resulted in no significant power output ($0.24 \mu\text{W cm}^{-2}$). Here we have demonstrated that the cell efficiency depends on the pitting corrosion of Al and the cell environment.

These power and current densities are much higher than those reported for glucose biofuel cell based on bilirubin oxidase and glucose oxidase derived from *Aspergillus niger* [49-51], enzyme-free glucose fuel cell [52] and glucose dehydrogenase biofuel cell [11]. Also, we have demonstrated a simple “green” method of using Al foil modified with ZnO as a reductant to the phosphate electrolyte and physiological saline electrolyte with Cl^- ions at room temperature to develop a single compartment hybrid Al/phosphate cell that can generate enough power that can be used for powering bio-implantable electronic devices or low powered electronic devices.

Figure 6 shows the stability of the cell performance operating in physiological saline buffer and 20 mM phosphate buffer under air-saturated conditions. Polarization curves of duplicate cells were obtained once a day for 2.5 weeks. After day 8, the buffers were exchanged every two days (indicated with $\downarrow$). An increase in current were observed as a result of the exchange of the spent physiological saline or phosphate buffer electrolyte for a fresh electrolyte. The results show good stability of the current density over the 2.5 weeks in physiological saline with approximately 28% drop in activity on day 9, where 100% activity is the current density at an external load of 3 k Ω at day 1. A 22% drop in activity was observed for the phosphate buffer cell at day 9. However, the phosphate buffer cell illustrates a limited lifetime of the cell, whereas the physiological saline buffer cell exhibited an overall stable current density profile. This stability in the profile could be attributed to the enhanced access to the active sites available for pitting via Cl^- ions in physiological saline buffer.

Experimental

Materials

Zinc chloride (99.99%), triethenamine (TEA, 99.99%), and all chemical reagents were purchased from Sigma-Aldrich and all supplementary chemicals were of analytical grades and used without further purification. All solutions were prepared with 18.2 M Ω cm Milli-Q water.

Electrode preparation

The Al/Au/ZnO electrode fabrication was previously reported [53]. Briefly, pure aluminium foil (Alfa Aesar, 99.9999%, 250 μm thick) was cut into pieces of approximately 1 cm x 0.5 cm and used as support substrates for the deposition of a thin film of gold and the subsequent hydrothermal growth of ZnO seed layers via a simple sol-gel process under mild conditions. Briefly, the ZnO precursors were prepared using zinc chloride and propanol. Triethenamine was added to the precursor solution to produce a final 0.1 M homogeneous ZnO nanosol, which was then aged. The ZnO seed layers were established on the Al substrate as a modifier via multiple dip-coating and annealing methods to form a thick layer of seeds. The resulting Al/Au/ZnO electrode was rinsed and dried overnight, in a desiccator. Recently, carbon-based cathodes, such as BuckyPaper has been used in lithium air cells [54]. Thus, BuckyPaper composed of compressed multiwalled carbon nanotubes (NanoTechLabs, Yadkinville, NC) was used as the cathode material (geometric area 0.25 cm^2).

Electrochemical Instrumentation and procedures

Electrochemical characterizations were conducted on BASi potentiostat/galvanostats EC Epsilon. All experiments were carried out at room temperature (25 ± 1 $^\circ\text{C}$). The electrochemical

experiments were performed in a conventional three-electrode cell with the exception of the fuel cell characterizations. The Ag/AgCl (KCl_{sat}) and platinum wire were used as the reference and counter electrode, respectively. The working buffer solution was 20 mM phosphate buffer. All potentials referenced in the present work are measured against Ag/AgCl reference electrode. Cyclic voltammetry were conducted with scan rates of 20 mV s^{-1} in air-saturated environment. The anode was further characterized using potentiostatic polarization curves generated by applying a series of potentials to the anode.

The cell characterizations were carried out in phosphate buffer (pH 7.4) and physiological saline buffer (pH 7.4, 0.137 NaCl, 20 mM phosphate) in air-saturated environment. The cell consisted of the Al/Au/ZnO anode and BuckyPaper cathode in the single compartment cell. The polarization curves for the cell was obtained from the use of a series of external loads (1 M Ω to 1 k Ω). The power density was obtained for the cell. Current densities were calculated using geometrical area of electrode.

After discharging the anode in the phosphate rich electrolyte, the morphology and structural characteristics of bare Al anode and as-fabricated ZnO modified Al anode (Al/Au/ZnO) were characterized by atomic force microscopy (AFM) using an Agilent 5500 Scanning Probe Microscope/ PicoView Software (Agilent Technologies, USA) and field-emission scanning electron microscopy (SEM, Hitachi SU-70) at 10 kV. The surface roughness root mean square (RMS) values were measured over 2×2 μm^2 areas for all samples. The elemental analysis of the byproduct were determined using X-ray photoelectron spectroscopy (XPS: Kratos Axis 165) at 10^{-8} to 10^{-9} Torr for the characterization of the $\text{Al}(\text{OH})_3$ and ZnHPO_3 composite high resolution scans of the $\text{Al}1s$, $\text{Al}2p$, $\text{P}2p$, $\text{Zn}2p$, $\text{O}1s$ and $\text{Cl}1s$ peaks. ^1H NMR and ^{31}P NMR measurements were performed on JEOL ECX 400 MHz NMR spectrometer. The trace Al, Zn and K elements in the byproduct were detected using inductively coupled plasma mass spectrometer (ICP-MS, PerkinElmer NexIon 300D with autosampler).

Conclusions

Here we present the activation of Al via ZnO nanocrystal modifier on Al/Au support electrode. Using hydrothermal growth and ZnO nanosol process, we demonstrate the activation of Al in the presence of phosphate rich electrolyte by inducing pitting corrosion on the surface of Al, which in turn accelerate the mobile defect species in the Al_2O_3 layer to sustain a continuous reaction with the water in the electrolyte. These results led to the use of Al/Au/ZnO as anodic platform combine with BuckyPaper cathode to realize a membraneless hybrid cell. We achieved an open-circuit voltage of 0.751 V and delivered a maximum power density of 1.77 mW cm^{-2} at a current density of 11.95 mA cm^{-2} in physiological saline buffer. The Al with ZnO modifier as a simple anodic material can serve as a good alternative to enzyme and/ or mediator based anodes because of its simplicity and it addresses the issues with the lack of efficient direct electron transfer due to large distance between the electrode surface and the enzyme active center, and limited number of enzyme molecules that can be electrically coupled to the electrode. However, further optimization of the reaction conditions could help realize further control of the open circuit voltage, current and power densities. A special feature of the constructed hybrid cell is that it generates hydrogen gas, high power output and provides clean electric energy production at room temperature and in physiological

saline buffer, thereby enabling an inexpensive route to construct a complete hybrid cell systems for bioelectronic devices.

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FIGURE LEGENDS:

Figure 1. Representative surface characterization of Al/Au/ZnO anode. (A) AFM micrograph (2 μ m x 2 μ m) of Al/Au and Al/Au/ZnO. (B) SEM micrograph of bare Al and Al/Au/ZnO anode after discharging in phosphate buffer and physiological saline buffer.

Figure 2. Reaction byproduct characterization: (A) ^{31}P NMR and ^1H NMR spectra of potassium phosphate buffer and $\text{Al}(\text{OH})_3$ and ZnHPO_3 composite; (B) XPS spectra of ZnHPO_3 and $\text{Al}(\text{OH})_3$ composite after discharging in physiological saline buffer solution; and (C) ICP characterization of trace elements via the dissolution of Al and Zn from $\text{Al}(\text{OH})_3$ and ZnHPO_3 composite.

Figure 3. (A) CV curves in phosphate electrolyte (pH = 7.4) on ZnO modified Al (Al/Au/ZnO) (black line), bare Al (grey line), and Al/Au (dotted line) under air-saturated condition. (B) CV curves of BuckyPaper cathode in phosphate electrolyte under H_2 -saturated (black line) and under O_2 -saturated (grey line) conditions. Scan rate: 20 mV s^{-1} .

Figure 4. Representative potentiostatic polarization curves of Al (■) and Al/Au/ZnO (●) electrodes.

Figure 5. (A) Schematic illustrating the reaction mechanism and (B) Current density-voltage and power density-current characteristics for Al/Au/ZnO at the anode and BP at the cathode, operating in phosphate buffer (•) and in physiological saline buffer (--) in air-saturated environment.

Figure 6. Stability of the cell performance operating in physiological saline buffer (—) and 20 mM phosphate buffer (·····) under air-saturated conditions. The buffers were exchanged every two days following day 8 (indicated with ↓). The current densities were taken at a constant load of 3 kΩ.

Graphical Abstract