ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

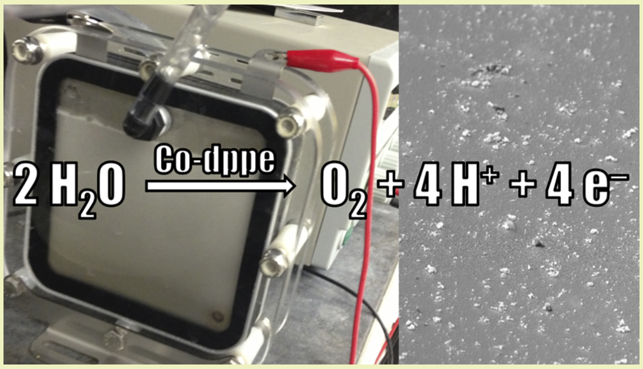
Performance Enhancement for Electrolytic Systems through the Application of a Cobalt-based Heterogeneous Water Oxidation Catalyst

Aaron J. Bloomfield,[†] Stafford W. Sheehan,[†] Samuel L. Collom,[†] and Paul T. Anastas*[,†,‡]

[†]Department of Chemistry, Yale University, 225 Prospect Street, PO Box 208107, New Haven, Connecticut 06520-8107, United States

[‡]School of Forestry and Environmental Science, Yale University, 195 Prospect Street, New Haven, Connecticut 06520-8107, United States

Supporting Information



ABSTRACT: We report a heterogeneous cobalt−phosphine-based water oxidation catalyst that was produced by thermal synthesis, and can be easily and rapidly deposited onto a variety of substrates from a suspension. Application of the catalyst dramatically improved the oxygen evolution efficiency and corrosion-resistance of stainless steel, nickel and copper anodes in alkaline media. More than 20 g of catalyst was prepared in a single batch, and it was shown to be effective at surface loadings as low as 20 μg/cm^2. The catalyst was investigated in three different systems: (1) An alkaline electrolyzer with stainless steel electrodes activated with the catalyst supported 120−200% of the current density of an unactivated but otherwise identical electrolyzer, over a range of applied potentials, and maintained this improved efficiency throughout 1495 h of continuous use in 1 M NaOH. (2) Copper anodes were activated and protected from corrosion in dilute sodium hydroxide for 8 h of electrolysis, before a steady decrease in performance over the next 48 h. (3) Activation of nickel anodes with the catalyst reduced the required overpotential by 90−130 mV at current densities between 7.5 and 15 mA/cm^2, thereby increasing the cell efficiency of water splitting as well as zinc deposition from alkaline zincate electrolytes. The cell efficiency for zinc deposition at a current density of 12.5 mA/cm^2 was improved from 68.0% with a nickel anode to 72.0% with 50 μg/cm^2 catalyst on the nickel anode.

KEYWORDS: *Water oxidation, Electrolysis, Water splitting, Energy storage, Zinc electrowinning, Zinc−air fuel cell, Electrocatalyst, Heterogeneous catalyst, Cobalt oxide, Copper anode, Green chemistry*

INTRODUCTION

There has been significant interest in the study of electrolytic energy storage to facilitate application of renewable energy technologies, which are otherwise of limited utility due to their intermittency.[1−5] Electrolysis of water is one established method for storing electrical energy in the form of hydrogen. Energy is released upon recombination of hydrogen with oxygen in a fuel cell or by combustion.[4,6−8] Similarly, electrolysis of zinc oxide shows significant potential for energy storage due to the significant energy density and power density of zinc-air batteries and fuel cells, as well as the abundance and nonhazardous nature of zinc.[9−11] Although the energy content of hydrogen is significantly higher than that of zinc on a mass basis (142 vs 5.3 MJ/kg), on a volume basis, even liquefied hydrogen is inferior to zinc (8.5 vs 38 MJ/L).[12] Technologies for electrolytic production of both hydrogen and zinc are currently too inefficient or too expensive to be economically viable on the scale required to meet global energy demand.[11,13] In both cases, anodic oxygen evolution is a major source of this inefficiency.[11,14,15]

Researchers at Lawrence Livermore reported an alkaline zinc generator that operated at approximately 77% efficiency, using nickel electrodes.[16] It should be noted that although primary zinc production is typically performed in acidic conditions because sulfuric acid is a byproduct of zinc ore processing, alkaline electrolysis is more efficient, requiring about 20% less electrical energy, and is therefore the preferred method for secondary zinc production processes such as zinc recycling and energy storage applications.[17] Alkaline electrolyzers typically produce hydrogen with between 40% and 65% energy efficiency,[6,8,13] which is not competitive with 70% to 80% round-trip efficiencies for pumped hydroelectric or compressed

Received: March 20, 2015
Revised: April 29, 2015
Published: May 5, 2015

DOI: 10.1021/acssuschemeng.5b00229
ACS Sustainable Chem. Eng. 2015, 3, 1234−1240

air energy storage.[6,18] High performance alkaline electrolyzers are capable of producing hydrogen with 80% energy efficiency,[6,19] but they require catalysts containing rare metals, such as platinum and ruthenium.[13,15] High efficiency acidic proton exchange membrane (PEM) electrolyzers also employ platinum, ruthenium or iridium catalysts,[20] due to the acid-instability of earth-abundant transition metal oxides.[14] These metals are expensive and energetically costly to produce,[21,22] and have been identified as materials of high criticality.[23]

Much research has been done on heterogeneous water oxidation catalysts based on first row transition metals,[24] including heterogeneous, carbon-containing cobalt oxides.[25−27] In our earlier reported work, a cobalt-based heterogeneous catalyst prepared with 1,2-bis(diphenylphosphino)ethane (hereafter referred to as Co-dppe) was found to be the most active water oxidation catalyst among a small library of catalysts prepared by the reaction of dicobalt octacarbonyl with neutral organo-phosphine and -amine ligands.[27] Co-dppe was found to be effective at surface loadings of <200 μg/cm^2, capable of supporting catalytic current at a potential of 1.51 V vs RHE in neutral borate electrolyte, and robust at potentials up to 1.6 V vs Ag/AgCl under neutral to highly alkaline conditions for more than 12 h.

In this paper, we report multi-gram-scale preparation of Co-dppe, demonstrate activity at loadings less than 50 μg/cm^2 (Figure S1 of the Supporting Information) and evaluate its performance in three different systems. Catalyst stability is tested in a commercially available, low-tech alkaline electrolyzer[28] over the course of 1495 h. Additionally, we examine the efficacy of Co-dppe on copper anodes in dilute sodium hydroxide, and find a significant increase in oxygen evolution efficiency with short-lived protection from corrosion during electrolysis. We also demonstrate the efficacy of Co-dppe in alkaline electrolytes containing high concentrations of dissolved zinc(II) species. In all cases, Co-dppe acts as an electrocatalyst for oxygen evolution at the anode, while the cathodic half reaction is either the reduction of protons to hydrogen gas, or in the case of zinc-containing electrolytes, the reduction of zinc(II) species to zinc metal.

EXPERIMENTAL SECTION

Synthesis of Co-dppe: A 250 mL round-bottom flask equipped with a large Teflon-coated stirbar and a reflux condenser sealed with a rubber septum was filled with dry nitrogen. The reflux condenser was removed, and dicobalt octacarbonyl (22.8 g) was added quickly, before replacing the condenser. The flask was flushed with dry nitrogen for 15 min. Xylenes (50 mL, sparged with nitrogen) was added by syringe, and the reaction mixture was stirred using a magnetic stirplate. Once the dicobalt octacarbonyl was fully dissolved, a stream of dry nitrogen was passed through the headspace of the reaction flask, and was vented through a bubbler. A suspension of 1,2-bis(diphenylphosphino)ethane (26.4 g) in xylenes (110 mL, sparged with nitrogen) was added quickly by cannula, and evolution of CO gas was observed. The reaction mixture was then heated to 160 °C (reaching reflux) and stirred vigorously for 1 h. The reaction vessel was then allowed to cool for 30 min before the condenser was removed. The reaction mixture was stirred vigorously, open to the air, for 4 days. The resulting heavy suspension was filtered using a Büchner funnel, and washed with ethyl acetate until the filtrate was colorless (ca. 3500 mL ethyl acetate). The remaining brown powder was dried under vacuum (<1 mmHg), yielding the catalyst (22.0 g).

Alkaline electrolyzer activation: A dry-cell alkaline electrolyzer[28] consisting of six stainless steel plates (two terminal plates and four bipolar plates), separated by 3 mm neoprene gaskets, was disassembled. A suspension of 224 mg of Co-dppe in 25.0 mL of ethyl acetate was sonicated for 45 s. 4.0 mL portions of the suspension were applied to one face of each of the four bipolar plates, and both faces of one of the terminals. After air-drying, these plates were reassembled such that the faces of the bipolar plates with catalyst were directed at the terminal plate without catalyst (see Figure S2 of the Supporting Information).

The electrolyzer was connected to a reservoir filled with 1.0 M NaOH electrolyte, and run at a constant current of 5.0 A (DC) for 62 days (1495 h). The electrolyte level was maintained by adding deionized water every two or 3 days, as needed, and the electrolyzer was drained, rinsed and refilled with new 1.0 M NaOH every 7 to 12 days. After each refill, the electrolyzer was subjected to a study in which the applied voltage was adjusted between 8.1 and 14.5 V (1.62−2.9 V/cell) in 0.20 V increments. The current was measured at each potential, and recorded. Another dry-cell alkaline electrolyzer[28] of the same dimensions, but without catalyst was filled with the same electrolyte each time, and used as a control for each study.

RESULTS AND DISCUSSION

Improving Traditional Alkaline Electrolysis. Although demonstrating utility over a long time course is an essential part of establishing industrial relevance, there are very few recent reports in scientific journals of electrodes tested for more than 100 h.[29−32] Therefore, having previously demonstrated stable activity of Co-dppe over 40 h of intermittent use,[27] we subjected the catalyst to electrolytic conditions continuously for 62 days.

Co-dppe was deposited (ca. 500 μg/cm^2) on the anodic faces of the stainless steel bipolar electrodes of a small, commercially available electrolyzer.[28] The electrolyzer was then charged with 1.0 M NaOH electrolyte, and operated at a fixed DC current of 5.0 A (ca. 35 mA/cm^2). To test whether or not detachment of active catalyst from the electrodes would be a plausible mechanism of deactivation, the electrolyte was drained and replaced with fresh 1.0 M NaOH about once per week. This procedure mimics the turnover of electrolyte in commercial systems and allows for analytical control of electrolyte concentration through the 62 day test. After each refill, the electrolyzer was subjected to a study in which the applied voltage was adjusted between 8.1 and 14.5 V (1.62−2.9 V/cell) in 0.20 V increments. The current was measured at each potential, and compared against a catalyst-free control electrolyzer of the same make and model, and was filled with electrolyte from the same batch used to refill the activated electrolyzer.

Figure 1 shows the increase in current density expressed as a percentage relative to the current density of the unactivated electrolyzer (Figure S3 of the Supporting Information shows individual current density data points). At voltages less than 1.7 V/cell, neither cell supported significant current density. At intermediate voltages (1.7−2.2 V/cell) there is a significant difference in current density due to the lower overpotential for the onset of water oxidation in the activated electrolyzer. At higher applied voltages, the current density is no longer limited by anodic water oxidation, and the current density asymptotically falls to ca. 120% as the applied voltage is increased. Interestingly, the performance enhancement observed with the activated electrolyzer became more substantial over the course of the study. Had catalyst degradation or leaching been a dominant mechanism, the electrolyzer performance would have diminished over the course of the study; an effect that would have been further exaggerated by the weekly electrolyte replacement.

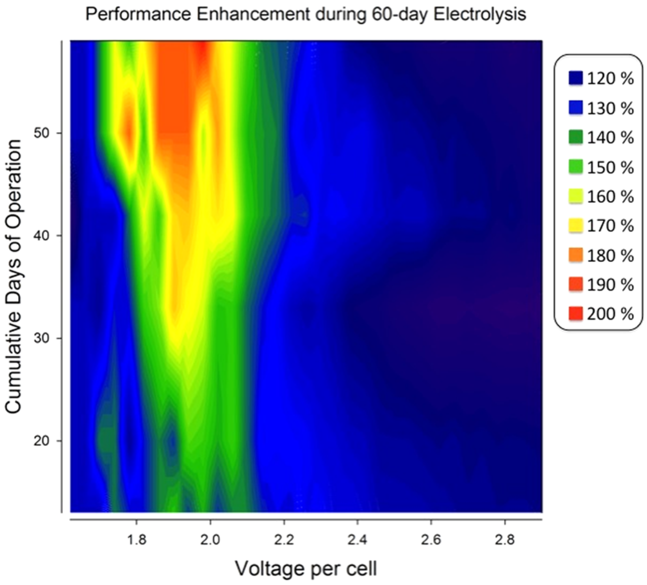


Figure 1. Performance enhancement of activated electrolyzer over the course of a 62 day electrolysis, expressed as the percentage of current density as compared to a catalyst-free electrolyzer.

After the 62nd day of continuous operation, the electrolyzer with catalyst was disassembled and the electrodes analyzed. Scanning electron microscopy (SEM) images showed discrete cobalt-containing particles still bound to the surface, although in significantly lower density than the initial surface loading (Figure S4 of the Supporting Information). No cobalt-containing film was observed on the electrodes, suggesting that no dissolution−electrodeposition processes occurred.[31] Analysis by XPS indicated the oxidation state and composition of the catalyst after electrolysis differed from the material initially deposited, similar to our previous observations.[27] That the performance of the electrolyzer improved with time suggests that the final material is more active under alkaline conditions. Ongoing collaborative investigation of the chemical, structural and morphological changes of the material during the course of electrolysis, using high-energy X-ray spectroscopy and computational methods, is the subject of a forthcoming paper.

In general, the activated electrolyzer supports at least 120% of the current density than the control electrolyzer across the entire working voltage range, and a maximum of 210% of the current density, observed at 1.98 V/cell on the final day of testing. This improvement is less significant than our previous single-cell measurements, which utilized platinum cathodes.[27] This is most likely because the cathodic faces of the bipolar plates were current-limiting, despite possessing the same geometric surface area as the anodic faces, because the overpotential for hydrogen evolution is higher on stainless steel than on platinum. Nickel is a more efficient proton reduction catalyst than stainless steel,[13] so we expect a more significant improvement with devices using nickel electrodes. In a single-cell experiment comparing activated and unactivated nickel anodes, each coupled with an unmodified nickel cathode, we observe that current density is nearly doubled with the addition of Co-dppe to the anode (Figure 2). The activity was maintained after 16 h of electrolysis at a potential of 1.25 V vs Hg/HgO, and there was no loss of activity after the working electrode was cycled rapidly (50 mV/s) between oxidizing (+1.35 V vs Hg/HgO) and reducing (−1.25 V vs Hg/HgO) potentials 5 times (see Figure S5 of the Supporting Information). SEM images of the electrode showed no major change in catalyst morphology after the potential cycling study.

Studies toward Enabling Copper as an Anode Material for Alkaline Electrolysis. Nickel or nickel-plated steel electrodes are standard in alkaline electrolyzers because

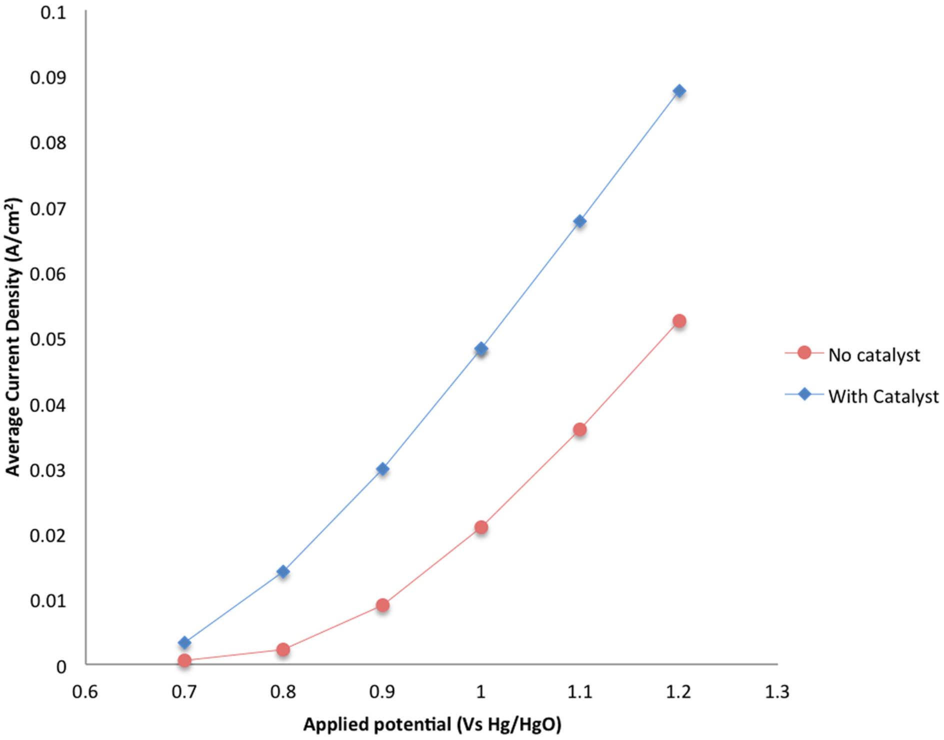


Figure 2. Comparison of nickel and Co-dppe/nickel anodes in 30 wt % KOH electrolyte at 24 °C.

Table 1. Comparison of Economic and Physical Profiles of Nickel and Copper as Electrode Materials

	nickel	copper
cost	6.82 US$/lb[35]	2.56 US$/lb[35]
production energy intensity	114 MJ/kg[36]	33 MJ/kg[36]
resistivity (293 K)	69.3 nΩ × m[37]	16.8 nΩ × m[37]
HER overpotential (1 mA/cm^2)	330 mV in 1 M NaOH[38]	340 mV in 0.15 M NaOH[39]
OER overpotential (1 mA/cm^2)	670 mV in 1 M NaOH[40]	corrodes competitively[33]

Table 2. Performance of Copper and Co-dppe/Copper Anodes

	bare Cu foil	Co-dppe on Cu (fresh)	Co-dppe on Cu (8 h old)	Co-dppe on Cu (44 h old)
Faradaic efficiency[a]	15 ± 5%	100 ± 3%	85 ± 3%	54 ± 5%
current density[b] (μA/cm^2)	263 ± 28	598 ± 18	534 ± 19	539 ± 12

[a] Determined by comparison of the volume of oxygen produced at the anode with the cumulative current passed during the time course. [b] Average current density measured during the second hour of each run, with error bars defined by three times the standard deviation of the measurements (see Figure S6 and related content in the Supporting Information).

nickel is a conductive metal that is highly corrosion resistant and a moderately active electrocatalyst for both hydrogen and oxygen evolution.[13] Copper is substantially less expensive to produce and machine than nickel, and is a significantly better electrical conductor and a similarly efficient hydrogen evolution catalyst (see Table 1). However, copper is known to be unsuitable as an anode material for alkaline electrolyzers because it is a poor catalyst for oxygen evolution and corrodes at a substantial rate at such oxidizing potentials.[33] It should be noted that a recent study has shown copper foil anodes to oxidize water in 1−2.5 M Na_2CO_3 electrolytes without significant corrosion.[34]

A suitable catalyst deposited on the copper anode could increase the rate of water oxidation and oxygen evolution relative to the rate of corrosion. Accordingly, copper electrodes with and without Co-dppe were compared as anodes for the electrolysis of 0.03 M NaOH electrolyte at 0.850 V vs an Hg/HgO reference electrode at room temperature. In the case of the unmodified copper anode, the Faradaic efficiency of oxygen evolution over the course of 8 h of electrolysis was determined to be approximately 15% by chronoamperometry and volumetric measurement of gas evolved at the anode (Table 2). Significant corrosion was observed and current density averaged approximately 263 μA/cm^2 over the second hour of the time course. An average for only a portion of the time course was chosen as the best measure due to degradation of the alkaline electrolyte by reaction with atmospheric carbon dioxide, thereby decreasing both pH and ion mobility of the electrolyte.[9] For further experimental details as well as a diagram of the experimental apparatus, see Figure S6 of the Supporting Information.

In contrast, the copper anode with Co-dppe deposited on the surface produced oxygen at ca. 100% Faradaic efficiency, and with more than twice the current density. After the initial 8 h electrolysis, the same catalyst-laden copper electrode was subjected to electrolytic conditions for an additional 36 h, after which the electrolyte was replaced, and electrolysis continued for a final 12 h. Although the catalyst-laden copper anode supported significantly greater current density throughout the study, the Faradaic efficiency decreased in each subsequent time course. SEM images of the electrode revealed some pitting in the copper, but catalyst particles containing Co, P and C persisted (see Figure S7 of the Supporting Information).

It appears that corrosion is nearly completely prevented initially, but that once started, the process continues with increasing rate. Because the corrosion resistance is only temporary, application of Co-dppe alone is insufficient to enable copper anodes for alkaline electrolysis. Perhaps slight modifications in electrolyte composition, temperature or a more uniform deposition may prevent the initiation of corrosion, thus allowing the use of copper as an anode material for water oxidation.

Water Oxidation Coupled with Zinc Reduction. Because Co-dppe increases the efficiency of oxygen evolution in alkaline electrolysis, and oxygen evolution is the major source of inefficiency in alkaline electrolytic zinc-based energy storage, the catalyst was evaluated in electrolytes containing high concentrations of zinc. Electrolysis of a solution prepared by dissolving 30 g of ZnO in one liter of 25 wt % NaOH produces oxygen gas at the anode and zinc metal at the cathode (>90% Faradaic yield of zinc). Cyclic voltammetry using a nickel foil anode or a nickel foil anode activated with Co-dppe (Figure 3) shows an improvement similar to that for water splitting with nickel electrodes under highly alkaline conditions, a 140 mV reduction in the potential required to achieve a current density of 10 mA/cm^2. In the case of the nickel anode activated with Co-dppe, increasing the zinc concentration to the saturation point increases the rate of reaction, while there is no discernible effect with the nickel-only anode. This indicates that, with electrodes of equal area, adding Co-dppe to the anode shifts the rate-limiting half-reaction from the anode to the cathode (note that at high currents the saturated zinc solution supports less current than the lower concentration, this is likely due to the lower ion mobility of $Zn(OH)_4^{2-}$ as compared to OH^-). Similarly, as the zinc depositions were performed for several hours at fixed potential, the current density at the enhanced anode was observed to increase with increasing cathode surface area, whereas the current density at the nickel-only anode was insensitive to increased cathode surface area, also indicating that without catalyst the anodic oxygen evolution half reaction was rate-limiting, while the cathodic reduction reaction was rate-limiting when coupled with an activated anode.

To assess the influence of Co-dppe on the efficiency of ZnO electrolysis, a series of 3 min chronoamperometric experiments were performed at a range of potentials, using both anode and cathode as working electrodes, measured against the same reference electrode (Figure 4a,b). In this way, the cell potential

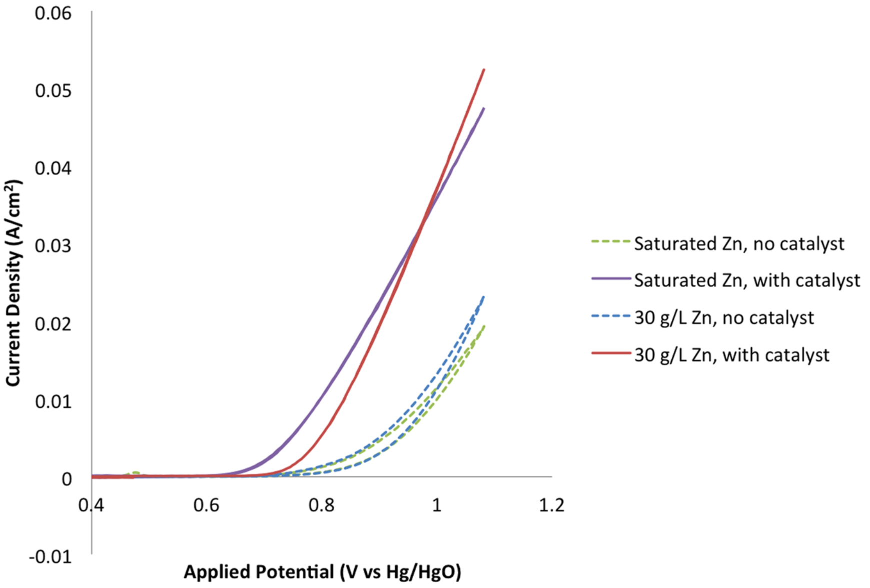


Figure 3. Cyclic voltammetry using nickel or Co-dppe/nickel anodes in 25 wt % NaOH electrolyte with ZnO at 23 °C.

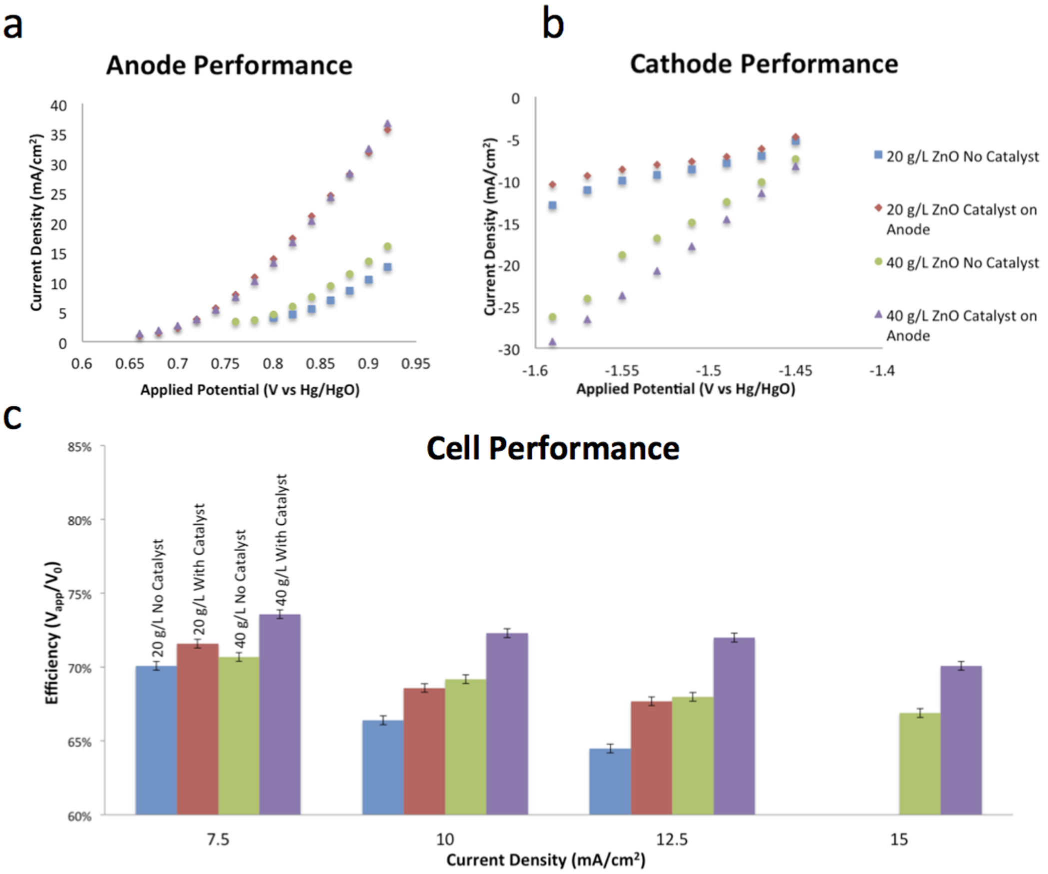


Figure 4. Anode, cathode and full-cell performance during alkaline electrolysis of zinc oxide.

and cell efficiency could be calculated for a range of current densities (Figure 4c). For this study, nickel foil electrodes were used as both anode and cathode, but the cathodic electrodes were plated with zinc immediately prior to evaluation to prevent proton reduction from interfering with the measurements. A loading of 50 μg Co-dppe/cm^2 was sufficient to demonstrate the effect.

As expected, anode performance was very sensitive to the presence of catalyst, and unaffected by zinc concentration (Figure 4a). Similarly, cathode performance was heavily influenced by the concentration of zinc in the electrolyte, but insensitive to the presence or absence of catalyst on the anode (Figure 4b). When compared to the unactivated nickel anode, the Co-dppe/Ni anode shows onset of current at a lower overpotential. The current density supported by the activated

DOI: 10.1021/acssuschemeng.5b00229
ACS Sustainable Chem. Eng. 2015, 3, 1234−1240

anode also increases more dramatically with increasing applied potential. For instance, in the more concentrated zinc electrolyte, the activated electrode can support a current density of 7.5 mA/cm^2 at an overpotential 90 mV lower than the nickel anode, and 15 mA/cm^2 at 130 mV less.

Using these data, the total voltage required for current densities of 7.5, 10, 12.5 and 15 mA/cm^2 were calculated. The cell efficiency was then calculated using the thermodynamic potential for alkaline zinc oxide electrolysis, 1.619 V.[16] Thus, it can be seen (Figure 4c) that in concentrated zinc electrolyte, operating at 70% efficiency (2.31 V), activation of the nickel anode doubles the current density. Considered another way, at a fixed current density of 15 mA/cm^2, activation allows the efficiency to increase from 66.9% to 70.1% (reduction in wasted energy from 33.1% to 29.9%). This difference may appear small, but a 10% reduction in the amount of energy wasted has significant influence on the economic and life-cycle analysis of energy storage methods.[41]

To assess the state of the catalyst after use in zinc-containing solutions, Co-dppe was deposited on FTO anodes and subjected to electrolysis for 12 h. SEM and SEM-EDX (energy-dispersive X-ray) analysis of the Co-dppe/FTO anodes indicated retention of catalyst particle morphology, and no incorporation of zinc (see Figure S8 of the Supporting Information). Additionally, the Co-dppe/FTO anodes retained their catalytic activity throughout the experiment, and showed no loss of activity for water splitting when assayed in a zinc-free sodium hydroxide solution afterward.

In summary, the electrocatalyst Co-dppe, which is easily synthesized from earth-abundant materials, was found to activate steel, nickel and copper anodes for electrolytic water oxidation, allowing both hydrogen and zinc production to proceed more efficiently. Stainless steel electrodes were shown to maintain improved activity for 1495 h of continuous use. Although corrosion of copper anodes was not completely prevented, copper anodes that were treated with the catalyst produced oxygen with nearly 100% Faradaic efficiency for 8 h and outperformed untreated copper anodes for over 50 h. Further development would be needed for catalyst-treated copper anodes to find practical application in alkaline electrolysis. That Co-dppe is prepared from earth-abundant materials, and can be quickly and easily deposited onto nickel, steel and copper electrodes to impart long-lived efficiency improvements at sub-milligram-per-square-centimeter loadings, suggests that this catalyst, or others like it, may enable electrolytic energy storage strategies to become economically viable ways of harnessing renewable energy on a global scale.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information as noted in text. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00229.

■ AUTHOR INFORMATION

Corresponding Author

*Paul T. Anastas. Address: Department of Chemistry, Yale University, 225 Prospect Street, PO Box 208107, New Haven, CT 06520-8107. Phone: (203) 432 5251. E-mail: paul.anastas@yale.edu.

Author Contributions

The paper was written through contributions of all authors. All authors have given approval to the final version of the paper.

Notes

The authors declare the following competing financial interest(s): U.S. Patent Application Number 14/322,773 has been filed for the intellectual property described in this paper.

■ ACKNOWLEDGMENTS

The authors acknowledge funding from an NSF Graduate Research fellowship (S. W. S.) and from the Yale Entrepreneurial Institute (research materials and devices). Facilities use was supported by the Yale Institute for Nanoscience and Quantum Engineering (YINQE) under NSF MRSEC-DMR-1119826. The authors thank Robert Crabtree, Charles Schmuttenmaer, the Center for Green Chemistry & Green Engineering at Yale, the Yale Solar Team and the Energy Sciences Institute, for their support.

■ REFERENCES

(1) U.S. Department of Energy Office of Science. Basic research needs for electrical energy storage, 2007, http://www.er.doe.gov/bes/reports/files/SEU_rpt.pdf.

(2) British Petroleum. BP statistical review of world energy, 2014, http://www.bp.com.

(3) Chu, S.; Majumdar, A. Opportunities and challenges for a sustainable energy future. *Nature* **2012**, *488* (7411), 294−303.

(4) Lewis, N. S.; Nocera, D. G. Powering the planet: Chemical challenges in solar energy utilization. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103* (43), 15729−15735.

(5) Armaroli, N.; Balzani, V. Towards a electricity-powered world. *Energy Environ. Sci.* **2011**, *4* (9), 3193−3222.

(6) Sternberg, A.; Bardow, A. Power-to-what? − Environmental assessment of energy storage systems. *Energy Environ. Sci.* **2015**, *8* (2), 389−400.

(7) Turner, J. A. Sustainable hydrogen production. *Science* **2004**, *305* (5686), 972−974.

(8) Dincer, I.; Acar, C. Review and evaluation of hydrogen production methods for better sustainability. *Int. J. Hydrogen Energy*, **2014**, http://dx.doi.org/10.1016/j.ijhydene.2014.12.035.

(9) Sapkota, P.; Kim, H. Zinc-air fuel cell, a potential candidate for alternative energy. *J. Ind. Eng. Chem.* **2009**, *15* (4), 445−450.

(10) Neburchilov, V.; Wang, H.; Martin, J. J.; Qu, W. A review on air cathodes for zinc-air fuel cells. *J. Power Sources* **2010**, *195* (5), 1271−1291.

(11) Li, Y.; Gong, M.; Liang, Y.; Feng, J.; Kim, J.; Wang, H.; Hong, G.; Zhang, B.; Dai, H. Advanced zinc-air batteries based on high-performance hybrid electrocatalysts. *Nat. Commun.* **2013**, *4*, 1805.

(12) Values calculated from heats of formation of $H_2O(g)$ and $ZnO(s)$ and density data found in: *CRC Handbook of Chemistry and Physics*, 95th ed.; CRC Press: Boca Raton, FL, 2014−2015; Section 4: Properties of the Elements and Inorganic Compounds, and Section 5: Thermochemistry, Electrochemistry, and Solution Chemistry, http://www.hbcpnetbase.com/ (accessed February 9, 2015).

(13) Marini, S.; Salvi, P.; Nelli, P.; Pesenti, R.; Villa, M.; Berrettoni, M.; Zangari, G.; Kiros, Y. Advanced alkaline water electrolysis. *Electrochim. Acta* **2012**, *82*, 384−391.

(14) Song, S.; Zhang, H.; Ma, X.; Shao, Z.; Baker, R. T.; Yi, B. Electrochemical investigation of electrocatalysts for the oxygen evolution reaction in PEM water electrolyzers. *Int. J. Hydrogen Energy* **2008**, *33* (19), 4955−4961.

(15) Rossmeisl, J.; Qu, Z.-W.; Zhu, H.; Kroes, G.-J.; Nørskov, J. K. Electrolysis of water on oxide surfaces. *J. Electroanal. Chem.* **2007**, *607* (1−2), 83−89.

(16) Cooper, J. F.; Krueger, R. *The Refuelable Zinc-Air Battery: Alternative Techniques for Zinc and Electrolyte Regeneration*; Report No.

UCRL-TR-218414; Lawrence Livermore National Laboratory (LLNL), U.S. Department of Energy: Livermore, CA, 2006.

(17) Brown, A. P.; Meisenhelder, J. H.; Yao, N. The alkaline electrolytic process for zinc production: A critical evaluation. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22* (2), 263−272.

(18) Denholm, P.; Kulcinski, G. L. Life cycle energy requirements and greenhouse gas emission from large scale energy storage systems. *Energy Convers. Manage.* **2004**, *45* (13−14), 2153−2172.

(19) Santos, D. M. F; Sequeria, C. A. C.; Figueiredo, J. L. Hydrogen production by alkaline water electrolysis. *Quim. Nova.* **2013**, *36* (8), 1176−1193.

(20) Sheehan, S. W.; Thomsen, J. M.; Hintermair, U.; Crabtree, R. H.; Brudvig, G. W.; Schmuttenmaer, C. A. A molecular catalyst for water oxidation that binds to metal oxide surfaces. *Nat. Commun.* **2015**, *6*, 6469.

(21) Ayres, R. U.; Peiró, L. T. Material efficiency: Rare and critical metals. *Philos. Trans. R. Soc., A* **2013**, *371* (1986), 20110563.

(22) Gutowski, T. G.; Sahni, S.; Allwood, J. M.; Ashby, M. F.; Worrell, E. The energy required to produce materials: Constraints on energy-intensity improvements, parameters of demand. *Philos. Trans. R. Soc., A* **2013**, *371* (1986), 2012003.

(23) Erdmann, L.; Graedel, T. E. Criticality of non-fuel minerals: A review of major approaches and analyses. *Environ. Sci. Technol.* **2011**, *45* (18), 7620−7630.

(24) Galan-Mascaros, J. R. Water oxidation at electrodes modified with Earth-abundant transition-metal catalysts. *ChemElectroChem* **2015**, *2* (1), 37−50.

(25) Hong, D.; Jung, J.; Park, J.; Yamada, Y.; Suenobu, T.; Lee, Y.; Nam, W.; Fukuzumi, S. Water-soluble mononuclear cobalt complexes with organic ligands acting as precatalysts for efficient photocatalyst water oxidation. *Energy Environ. Sci.* **2012**, *5* (6), 7606−7616.

(26) Ressnig, D.; Shalom, M.; Patscheider, J.; More, R.; Evangelesti, F.; Antonietti, M.; Patzke, G. R. Photochemical and electrocatalytic water oxidation activity of cobalt carbodiimide. *J. Mater. Chem. A* **2015**, *3*, 5072−5082.

(27) Bloomfield, A. J.; Sheehan, S. W.; Collom, S. L.; Crabtree, R. H.; Anastas, P. T. A heterogeneous water oxidation catalyst from dicobalt octacarbonyl and 1,2-bis(diphenylphosphino)ethane. *New J. Chem.* **2014**, *38* (4), 1540−1545.

(28) 6-inch dry cell kits (product code ACRES02) purchased from Advanced HHO, http://www.AdvancedHHO.com/.

(29) Solmaz, R.; Dörner, A.; Kardas, G. The stability of hydrogen evolution activity and corrosion behavior of NiCu coatings with long-term electrolysis in alkaline solution. *Int. J. Hydrogen Energy* **2009**, *34* (5), 2089−2094.

(30) Hansen, R. E.; Das, S. Biomimetic di-manganese catalyst cage-isolated in a MOF: Robust catalyst for water oxidation with Ce(IV), a non-O-donating oxidant. *Energy Environ. Sci.* **2014**, *7* (1), 317−322.

(31) Esswein, A. J.; Surendranath, Y.; Reece, S. Y.; Nocera, D. G. Highly active cobalt phosphate and borate based oxygen evolving catalysts operating in neutral and natural waters. *Energy Environ. Sci.* **2011**, *4*, 499−504.

(32) Shaner, M. R.; Hu, S.; Sun, K.; Lewis, N. S. Stabilization of Si microwire arrays for solar-driven H_2O oxidation to $O_2(g)$ in 1.0 M KOH(aq) using conformal coatings of amorphous TiO_2. *Energy Environ. Sci.* **2015**, *8* (1), 203−207.

(33) Miller, B. Split-ring disk study of the anodic processes at a copper electrode in alkaline solution. *J. Electrochem. Soc.* **1969**, *116* (12), 1675−1680.

(34) Du, J.; Chen, Z.; Ye, S.; Wiley, B. J.; Meyer, T. J. Copper as a robust and transparent electrocatalyst for water oxidation. *Angew. Chem., Int. Ed.* **2015**, *54* (7), 2073−2078.

(35) Exchange spot prices as reported on www.kitcometals.com at 11:38 AM on February 9, 2015.

(36) Norgate, T. E.; Rankin, W. J. Life cycle assessment of copper and nickel production. *Proceedings, Minprex 2000, International Conference on Minerals Processing and Extractive Metallurgy*, Melbourne, Victoria, September 11−13, 2000; International Congress on Mineral Processing and Extractive Metallurgy: Carlton, Australia, 2000; pp 133−138.

(37) *CRC Handbook of Chemistry and Physics*, 95th ed.; CRC Press: Boca Raton, FL, 2014−2015; Section 12: Properties of Solids, http://www.hbcpnetbase.com/ (accessed February 9, 2015).

(38) Lasia, A.; Rami, A. Kinetics of hydrogen evolution on nickel electrodes. *J. Electroanal. Chem.* **1990**, *294* (1−2), 123−141.

(39) Bockris, J. O'M.; Pentland, N. The mechanism of hydrogen evolution at copper cathodes in aqueous solutions. *Trans. Faraday Soc.* **1952**, *48*, 833−839.

(40) Lyons, M. E. G.; Brandon, M. P. A comparative study of the oxygen evolution reaction on oxidized nickel, cobalt and iron electrodes in base. *J. Electroanal. Chem.* **2010**, *641* (1−2), 119−130.

(41) Rydh, C. J.; Sandén, B. A. Energy analysis of batteries in photovoltaic systems. Part II: energy return factors and overall battery efficiencies. *Energy Convers. Manage.* **2005**, *46* (11−12), 1980−2000.