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Air-Breathing Laminar Flow-Based Direct Methanol Fuel Cell with Alkaline Electrolyte

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We report the performance of an air-breathing laminar flow-based fuel cell (LFFC) operated in alkaline and acidic media. These direct methanol fuel cells exhibit open-circuit potentials of 0.93 and 1.05 V in acidic and alkaline media, respectively, demonstrating the absence of methanol crossover in both media. The LFFCs perform better in alkaline media under identical reaction conditions due to improved reaction kinetics at high pH. Further electrochemical investigation of these differences in reaction kinetics at the anode and cathode is also reported.

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Microfuel cells have the potential to achieve higher energy densities than batteries and have thus received intense investigation as a power source for a wide range of portable applications. Extensive research efforts are focused on the development and miniaturization of promising fuel cell technologies, including direct methanol fuel cells (DMFCs) and polymer electrolyte membrane-based fuel cells (PEMFCs, operated with hydrogen/oxygen).¹⁻³ In most fuel cells, a polymer electrolyte membrane such as Nafion allows protons to diffuse from the anode to the cathode, while trying to prevent fuel molecules from diffusing across and mixing with oxygen at the cathode. Poor performance or a lack of selectivity by the membrane leads to a key performance-limiting process called fuel crossover that has plagued the PEM-based fuel cells. In addition to fuel crossover, cathode flooding and anode dry-out (water management) due to osmotic drag of water molecules associated with protons diffusing from the anode to the cathode, as well as due to the formation and consumption of water at the cathode and anode, respectively, impedes the performance and commercial implementation of these fuel cells.⁴

To avoid some of these membrane-related issues, we as well as others are investigating laminar flow-based fuel cells (LFFCs), that operate with a range of fuels including formic acid/O₂, H₂/O₂, and vanadium redox couples.⁵⁻⁸ In these microfluidic fuel cells, the anode and the cathode streams flow parallel to each other in direct liquid/liquid contact. In a laminar flow regime, fuel mixing in these streams is limited to the slow process of molecular diffusion. The LFFC design offers the following advantages: (i) fuel crossover can be prevented by adjustment of the flow rates of each of the streams since they set the width of the diffusional mixing zone at the interface of the two streams; (ii) the continuously flowing aqueous electrolyte avoids water management issues; (iii) each LFFC can be operated in either alkaline or acidic media without any change to the cell other than the pH of the streams.^{9,10} Until recently, these LFFCs were severely performance limited at the cathode due to poor solubility and low diffusivity of oxygen in aqueous media. We have overcome these limitations by the incorporation of an air-breathing gas diffusion electrode (GDE) as the cathode, which resulted in a fivefold improvement in maximum power density of LFFCs operated with formic acid as the fuel.¹¹

While hydrogen fuel cells or direct liquid fuel cells operating in acidic media have been extensively studied, those operating in alkaline media have received much less attention although (i) studies indicate that reaction kinetics of both fuel oxidation at the anode,¹² especially CO oxidation¹³ and the oxygen reduction reaction (ORR)

at the cathode^{14,15} are more facile in alkaline media; and (ii) non-noble metal catalysts such as nickel (at the anode) and silver (at the cathode) can potentially replace the presently used Pt-based catalysts when operating in alkaline media.¹⁶⁻¹⁸ Whereas in polymer electrolyte membrane-based fuel cells or common direct methanol based fuel cells protons that are formed at the anode diffuse through the electrolyte membrane (typically protonated Nafion) to the cathode, in alkaline hydrogen or direct methanol fuel cells hydroxyl ions that are formed at the cathode diffuse to the anode through an anion-exchange membrane designed for alkaline fuel cells.¹⁶ This leads to two additional challenges for fuel cells operated in alkaline media: first, at the anode the hydroxyl ions can react with the generated carbon dioxide or atmospheric carbon dioxide to form carbonates that can precipitate over time and clog the pores of the membrane and the catalyst layer. This challenge can be avoided by using ultra-pure hydrogen and oxygen as the fuel, as, for example, used by NASA in fuel cells for the Apollo Space Shuttle program. Second, the conductivity of alkaline anion exchange membranes designed for fuel cells is lower than that of protonated Nafion membranes.¹⁶

In earlier work, we, as well as others, have shown that LFFCs can be operated in both acidic and alkaline media,^{9,10} and that fuel crossover can be avoided.^{6,8} Also, any carbonates formed when operating in alkaline media are immediately removed by the flowing electrolyte. The LFFCs used in those studies were still significantly mass-transfer limited at the cathode, so the suggested benefits of enhanced kinetics attributed to alkaline media could not be observed. Here, we report and compare the performance of air-breathing direct methanol LFFCs operating in either alkaline or acidic media, to show how the improved reaction kinetics of methanol oxidation and ORR in alkaline media leads to improved fuel cell performance.

Experimental

Electrode preparation.— Graphite plates (5 mm thick) with three holes (two inlets, and one outlet) were used as the anode. A 2 mm thick polymethylmethacrylate (PMMA) separator with a window of length 3 cm and width 3 mm was attached with 5 min epoxy (Devcon, MA) to the graphite anode. A catalyst ink comprised of 10 mg/cm² of Pt–Ru 50:50 atom wt % alloy (Alfa Aesar) and 1.5 mg/cm² of Nafion was added onto the exposed area of the graphite plate (anode) and polyethylene tubes were mounted in the inlet and outlet holes and secured in place with glue. A sheet of Toray carbon paper with a platinum loading of 0.35 mg/cm² using 10% Pt on Vulcan XC 72 from E-TEK (Somerset, NJ) as well as an additional layer of catalyst ink with a Pt (Alfa Aesar) loading of 2 mg/cm² and 0.1 mg/cm² of Nafion was used as the cathode. The gas-diffusion electrode was positioned on top of the PMMA window to cover the microfluidic channel and the assembly was held to-

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gether using paper binder clips (Highmark), which also prevented bulging of the GDE. The geometrical surface area of both electrodes used in this study was 0.66 cm^2 . We reported a detailed fabrication procedure of this air-breathing LFFC previously.¹¹

Fuel cell testing.—The fuel cell assembly was tested using acidic (anode stream: 1 M MeOH + 0.5 M H_2SO_4 , cathode stream: 0.5 M H_2SO_4) or alkaline (anode stream: 1 M MeOH + 1 M KOH, cathode stream: 1 M KOH) streams. Polarization curves were obtained by measuring the current at different cell potentials after steady state was reached. Using an external Ag/AgCl reference electrode (in 3 M NaCl, BAS, West Lafayette, IN), as reported earlier,¹⁹ we also recorded the cathode potential for each applied cell potential. The anode potential could then be obtained by taking the difference between the cell potential and the cathode potential.

Single electrode studies.—Single electrode studies of the individual anode and the cathode as used in the fuel cell tests were performed using cyclic voltammetry (CV) and chronoamperometry (CA). The anode was electrochemically cleaned by cycling the electrode from 0.05 to 1.5 V vs RHE at a scan rate of 500 mV/s in 0.5 M H_2SO_4 or 1 M KOH. The anode was then cycled at a scan rate of 10 mV/s from 0 to 1.1 V vs RHE in 1 M MeOH + 0.5 M H_2SO_4 or 1 M MeOH + 1 M KOH solution purged with argon. The chronoamperometric data was recorded by holding the anode at 0.3, 0.5, and 0.7 V vs RHE for 300 s. The cathode was electrochemically characterized using chronoamperometry, with the potential held at 0.8, 0.7, and 0.6 V vs RHE in 0.5 M H_2SO_4 or 1 M KOH solution saturated with O_2 gas, and the currents were measured as a function of time.

Results and Discussion

Here we study and compare the performance of an air-breathing direct methanol LFFCs operated in acidic or alkaline media at room temperature. Figure 1a shows polarization curves for the LFFCs operated in acidic and alkaline media under identical operating conditions. Typical open circuit potentials (OCPs) reported for miniaturized direct methanol fuel cells (e.g., DMFCs) range from 0.5 to 0.8 V,¹⁻³ while the OCPs for the acidic and alkaline LFFCs studied here are significantly higher, 0.93 and 1.05 V, respectively. These high OCPs indicate that methanol crossover can be minimized in these LFFCs when operated under these conditions. The polarization curves also indicate that the performance of LFFCs operated in acidic or alkaline media is similar at higher cell potentials ($>0.5 \text{ V}$) when the current densities are still low. At cell potentials below 0.5 V, however, the measured current densities of LFFCs run in alkaline media are at least 40% higher than those for LFFCs run in acidic media. The better performance of LFFCs operated in alkaline media is also apparent from a comparison of the power density curves (Fig. 1b). A maximum power density of 11.8 and 17.2 mW/cm^2 , respectively, were found for operation in acidic or alkaline media, respectively. In comparison, the power densities obtained with miniaturized conventional DMFCs reported in the literature are similar, ranging from 2 to 15 mW/cm^2 .¹⁻³

A number of factors can potentially contribute to the differences in performance observed for LFFCs operated with fuel and oxidant streams of different pHs. Differences in the exact cell geometry and catalyst loading can be excluded since the same cell was operated in alkaline and acidic media to record the respective polarization curves. The sole difference is the fact that both the cathode and the anode stream contain either 0.5 M H_2SO_4 (acidic) or 1 M KOH (alkaline). Factors that can contribute to the observed differences in LFFC performance are differences in (i) reaction kinetics, (ii) electrolyte conductivity, and/or (iii) mass transfer (e.g., the rate of boundary layer replenishment), and each is discussed now in more detail.

Conductivity.—The bulk ionic conductivity of aqueous solutions of 0.5 M H_2SO_4 and 1 M KOH at 25°C are comparable since both

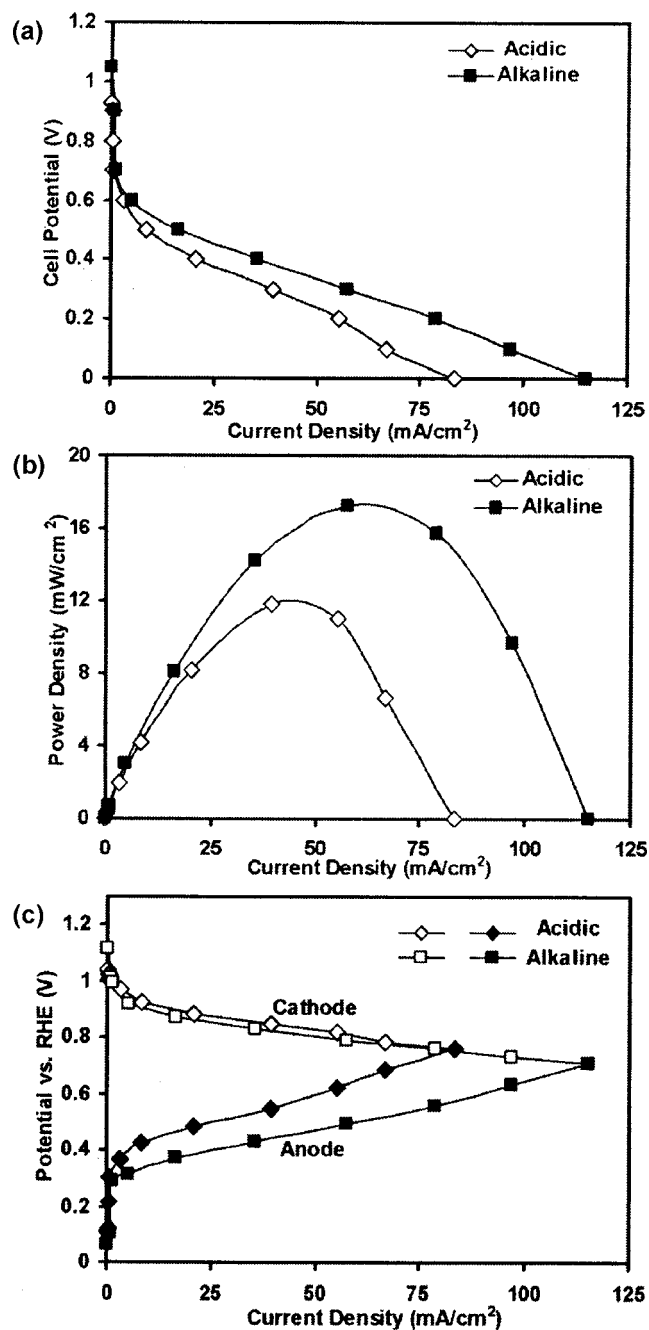


Figure 1. (a) Polarization curves, (b) power density curves, and (c) anode and cathode potentials vs RHE for an air-breathing, direct-methanol LFFC operated in either alkaline or acidic media at room temperature.

are on the order of 0.2 S/cm ,²⁰ so the difference in performance is not due to the difference in bulk ionic conductivity. We further analyzed the conductivity and resulting cell resistance of the LFFC studied here. Based on an anode to cathode spacing of 2 mm a solution resistance of $1 \Omega \text{ cm}^2$ can be calculated. Using the maximum current density measured (120 mA/cm^2 ; Fig. 1a) and the solution resistance results in a calculated maximum ohmic overpotential difference of only 120 mV from the theoretical potentials. In comparison, the conductivity of fully hydrated Nafion, the electrolyte in more conventional methanol fuel cells (e.g., DMFCs), is significantly lower, 0.1 S/cm ,²¹ yet the much smaller electrode to

electrode distance (50–178 μm) limits the ionic resistance to 0.2 to 1.3 $\Omega\text{ cm}^2$,^{19,22-24} similar to the ionic cell resistances encountered in these LFFCs.

Mass transfer.— Mass transfer of several species to and from the electrodes is required during fuel cell operation. These species include hydronium ions (acidic fuel cell), hydroxide ions (alkaline fuel cells), oxygen, and methanol. Transport of hydronium and hydroxide ions is not expected to be a limiting factor, since the diffusivities of these species are exceptionally high 9.31×10^{-5} and $5.28 \times 10^{-5}\text{ cm}^2/\text{s}$, respectively,²⁵ while migration also contributes to their transport.

Oxygen mass transport was a limiting factor in earlier generations of LFFCs,¹⁰ because of the low solubility (0.84 mM in 1.0 M KOH and 1.14 mM in 0.5 M H_2SO_4 ²⁶) and low diffusivity ($1.5 \times 10^{-5}\text{ cm}^2/\text{s}$ in 1.0 M KOH²⁷ and $1.8 \times 10^{-5}\text{ cm}^2/\text{s}$ in 0.5 M H_2SO_4 ²⁸) of oxygen in the electrolyte solutions. These levels of solubility and diffusivity are too low to supply oxygen by diffusion through a millimeter-scale aqueous stream. Incorporation of a GDE as the cathode created an air-breathing LFFC in which the rate of oxygen transport is dramatically increased.¹¹ Although oxygen reduction at the cathode still requires absorption of oxygen from air ($\sim 21\%$ oxygen) into the electrolyte and diffusion to the cathode catalyst, the thinner solution layer in the GDE, on the order of micrometers, facilitates a higher rate of oxygen transport than in the previous generation LFFC in which the electrolyte was presaturated with pure oxygen. High rates of oxygen transport to the cathode are confirmed by the shape of the cathode polarization curves (Fig. 1c), which demonstrate the lack of oxygen transport limitations.

The diffusivity of methanol in dilute aqueous solutions ($\sim 1.5 \times 10^{-5}\text{ cm}^2/\text{s}$ ²⁹) is similar to that of oxygen, but the methanol concentration is three orders of magnitude larger than that of oxygen. Therefore, methanol transport is not expected to be a limiting factor. The shape of the anode polarization curves (Fig. 1c) confirms the lack of methanol transport limitations (Fig. 1c).

In sum, mass transfer at both the anode and cathode can be excluded as a source of performance limitations, irrespective of operation in alkaline or acidic media.

Reaction kinetics.— The higher current densities observed when operating in alkaline media can also be due to improved kinetics of methanol oxidation and/or oxygen reduction. Further analysis of the individual anode and cathode potentials (Fig. 1c) reveals that the enhanced performance stems mainly from lower anode overpotentials at a given current density.

To further support this observation we characterized the individual anode and cathode in acidic and alkaline media in an electrochemical cell to understand the kinetics of the individual electrodes in each of these media. Figure 2 shows the cyclic voltammetry (CV) data for the anode recorded in 1 M MeOH in 0.5 M H_2SO_4 or in 1 M KOH. Methanol oxidation in alkaline media starts at a much lower potential than in acid media. Moreover, the current densities due to methanol oxidation in alkaline media are higher than those observed in acidic media. Chronoamperometry (CA) data, collected by holding the electrode at 0.3, 0.5, and 0.7 V vs RHE, confirmed these trends. The methanol oxidation currents are, depending on the applied potential, 2.5 to 7.5 times higher in alkaline media (Fig. 3). This observation of superior methanol oxidation in alkaline media is in agreement with prior electrochemical studies by Tripkovic et al.^{12,30,31} The CO formed during methanol oxidation is further oxidized by surface-adsorbed OH, which is formed as a result of the decomposition of water in acid media yet by simple adsorption from solution in alkaline media. Even in the absence of specifically adsorbing anions that compete with OH^- , solutions of low pH adsorb smaller amounts of OH.^{32,33} In sulfuric acid solutions, sulfate/bisulfate adsorption may reduce OH adsorption.^{12,13,30,31,34}

The performance of the individual cathodes in the LFFC operated in acidic and alkaline media (Fig. 1c) is identical within error margins. Earlier studies have demonstrated that oxygen reduction is

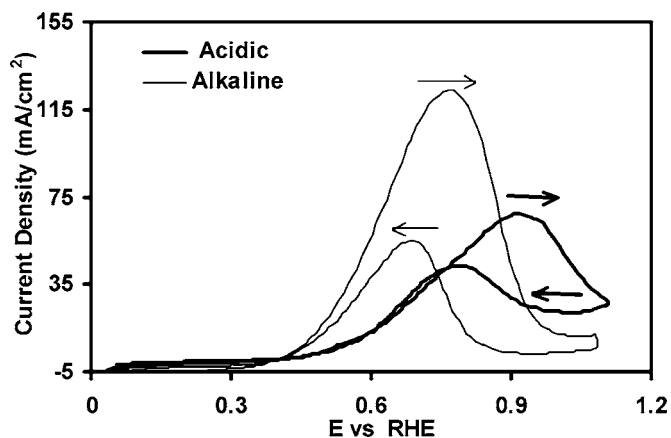


Figure 2. CV data for the anode in the presence of 1 M MeOH recorded in either 0.5 M H_2SO_4 or in 1 M KOH. The electrodes were cycled at a scan rate of 10 mV/s.

faster in alkaline media.^{14,15} A CA study on the cathode used in this investigation indeed showed about 20% higher current densities for oxygen reduction when holding the potential at 0.8, 0.7, or 0.6 V vs RHE in 1 M KOH compared to 0.5 M H_2SO_4 (Fig. 4). Note, however, that these electrochemical studies on the cathode were performed using dissolved oxygen, and thus were limited by oxygen transport, whereas the LFFC experiments were performed with an air-breathing cathode. In future LFFCs in which the anode limitation has been addressed, the benefit of improved oxygen reduction kinetics in alkaline media may lead to an even larger performance enhancement of LFFCs operated in alkaline compared to acidic media.

Conclusions

In this paper we compare the performance of an air-breathing direct methanol LFFC operated in either alkaline or in acidic media. High OCPs of 1.05 and 0.93 V, respectively, are observed, which indicate control over methanol crossover. Higher current densities are observed for the cell when operated in alkaline media. In the present LFFCs, this enhancement is due to better performance of the anode. Individual electrochemical characterization of the anode and the cathode used in the LFFC studied here showed that reaction kinetics is better in alkaline media for both methanol oxidation and oxygen reduction, in accordance with the literature.^{12,35}

In the LFFCs studied here, the observed improvement in overall cell performance can be attributed to improved reaction kinetics at the anode. The anode and cathode polarization curves indicate that the LFFCs are still both anode and cathode limited. Upon addressing these limitations, improvement of the overall cell performance when switching from acidic to alkaline media could potentially be even more than the present gain of about 40% in maximum current and power densities. The high OCP of the LFFC in alkaline media eliminates the need for development of an appropriate polymer electrolyte membrane that allows hydroxyl ions to diffuse across. Moreover, another key issue that has hampered the development of alkaline fuel cells to date, clogging of pores in the membrane and catalysts due to carbonate formation, is absent in the LFFCs studied here. While carbonates are formed, they are immediately washed away and could be filtered out of the solution in a system design that would involve recirculation of the streams. In addition, any electrolyte consumed due to reaction with the generated carbonates could be replenished in such a recirculation loop. Finally, the Pt-based catalyst can potentially be replaced with cheaper and readily available non-noble metals such as a nickel anode or silver cathode when operating in alkaline media.

In sum, LFFCs will eventually enable a significant performance enhancement of micro fuel cell-based power sources by taking ad-

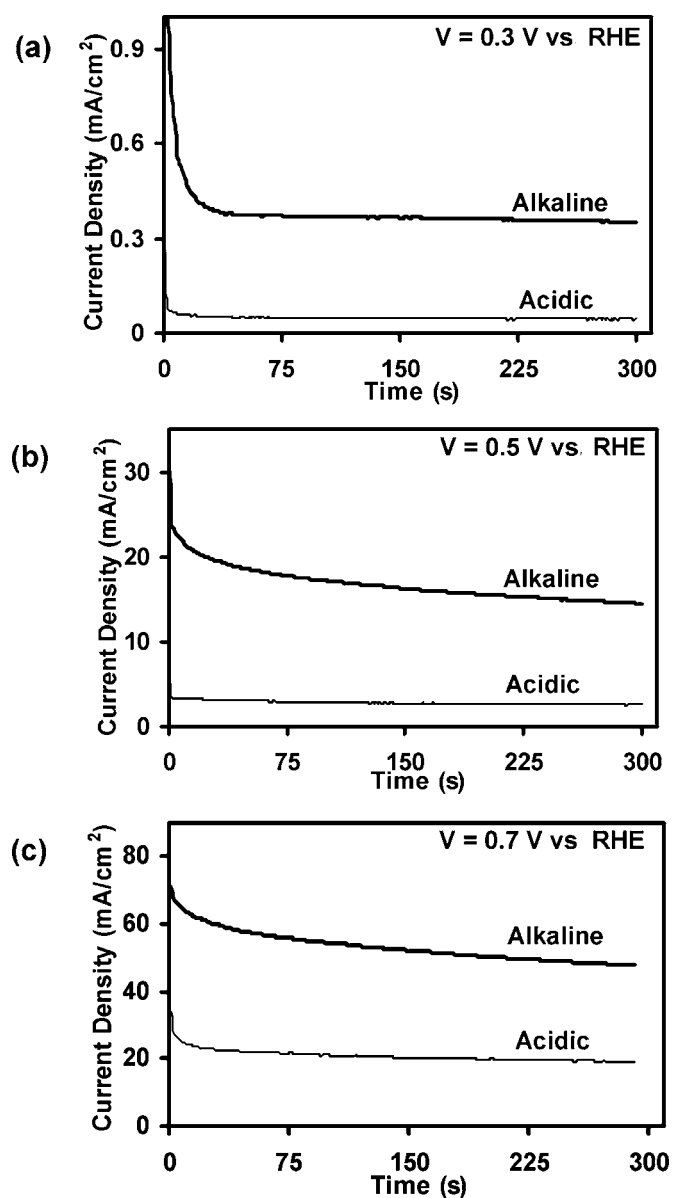


Figure 3. CA data of the anode for electro-oxidation of 1 M MeOH recorded at (a) 0.3, (b) 0.5, and (c) 0.7 V vs RHE in either 0.5 M H₂SO₄ or 1 M KOH media.

vantage of improved reaction kinetics when operated in alkaline media as opposed to acidic media, without facing the issue of carbonate formation.

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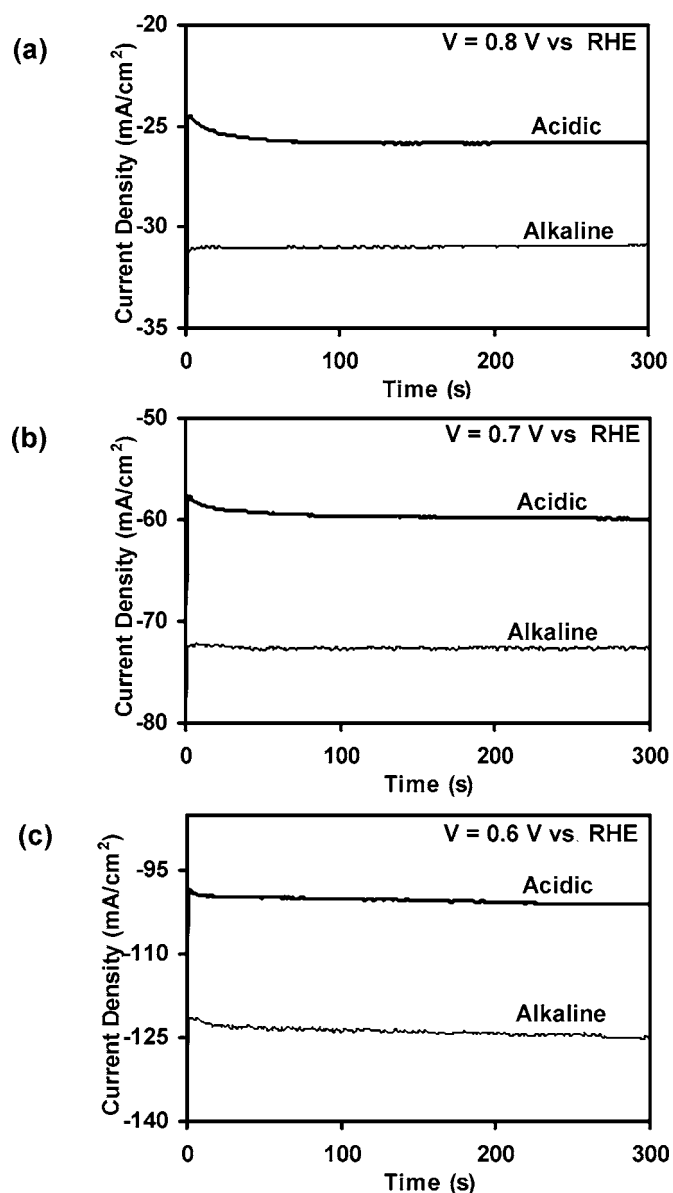


Figure 4. CA data of the cathode for electroreduction of oxygen recorded at (a) 0.8, (b) 0.7, and (c) 0.6 V vs RHE in either 0.5 M H₂SO₄ or 1 M KOH media saturated with O₂.

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