Electronic Supplementary Information

Enhancing Alcohol Electrocatalysis with the Addition of Magnetic Composites to Nickel Electrocatalysts

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Experimental

Preparation of tetrabutylammonium bromide (TBAB) modified Nafion® and coating of Toray electrodes: Protons in Nafion (Nafion perfluorinated resin solution, Aldrich) are exchange with TBA^+ ions from TBAB(Fluka, puriss, 99.0 %) as per the literature procedure described in Kloztbach et. al.[1] This provides an environment with increased transport, decreased ion selectivity, and decreased pH. For drop casting on Ni^{2+} deposited Toray paper electrodes, this TBAB modified Nafion suspension was prepared and mixed in the following ratios: 50:15:35 TBAB modified Nafion suspension: Bangs magnetic microparticles in saline suspension (magnetite microparticles coated with chemically and electrochemically inert coating and having an average diameter of 3.19um, Bang Laboratories, Inc.): 35 mL absolute ethanol. Control composites are 50:50 TBAB modified Nafion suspension: 50 mL absolute ethanol.

A volume of 12 µL of casting solutions are drop cast onto both TBAB control electrodes and magnetically modified composite electrodes (referred to here after as BANGS electrodes) to create a uniform film. The magnetic composite electrodes are dried initially for 10 minutes within a permanent magnetic field to orient the particles (NdFeB ring magnet, OD = 3 in, ID = 2 in, h = 0.25 in). The cast electrodes are allowed to dry overnight before additional electrochemical evaluation. Magnetic microparticles are approximately 17 % (v/v) of the final dried film.

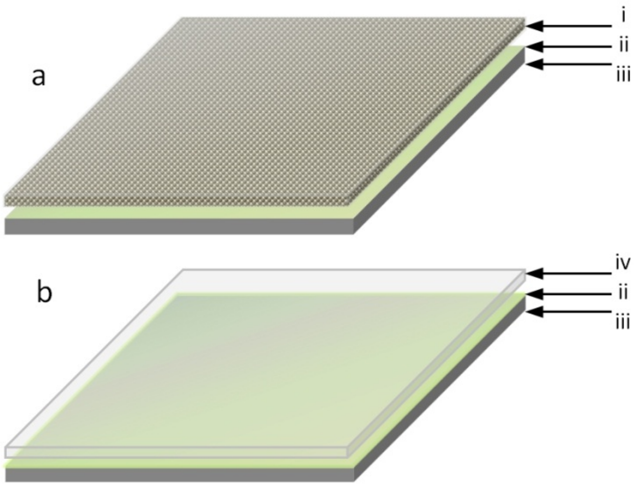

Figure S1. Composite electrode schemes, (a.) Magnetic composite, i magnetic microparticles in tetrabutylammonium bromide (TBAB) modified Nafion® film (~ 16μm), ii electrodeposited Ni^{2+}, and iii Toray paper;(b.) iv Control TBAB modified Nafion composite, ii electrodeposited Ni^{2+}, iii Toray paper.

Surface Microscopy

Bangs particles, as a volume fraction of TBAB modified Nafion, are approximated at 17 % (v/v). Dry films, as imaged by scanning electron microscopy (SEM), reveal an even distribution of particles on the electrode surface, as shown in Figure S2 and S3. The SEM images, do however, show that magnetic composite films, after electrochemical characterization, retain their structure, which implies long term stability of the system. SEM samples were prepared by adhering Toray paper electrodes to an aluminum stub with adhesive carbon paper. No surface sputtering was performed. All images were taken using a FEI NanoNova SEM.

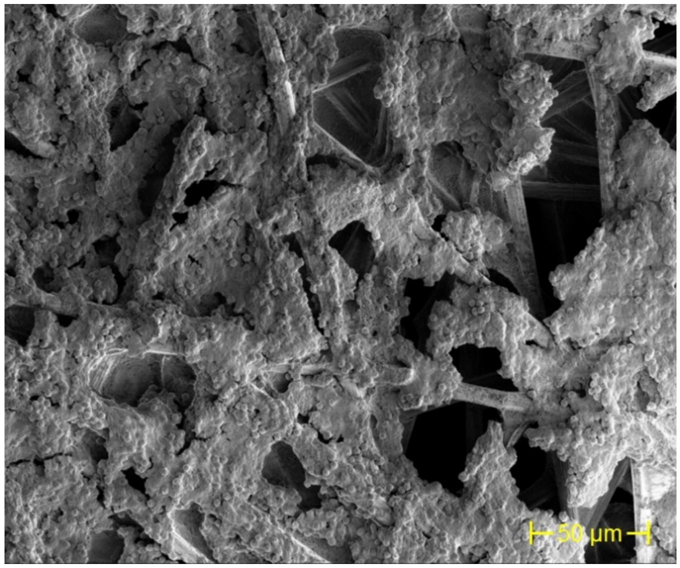

Fig. S2. SEM of magnetic composite on Toray paper at 1000x magnification, 1 keV

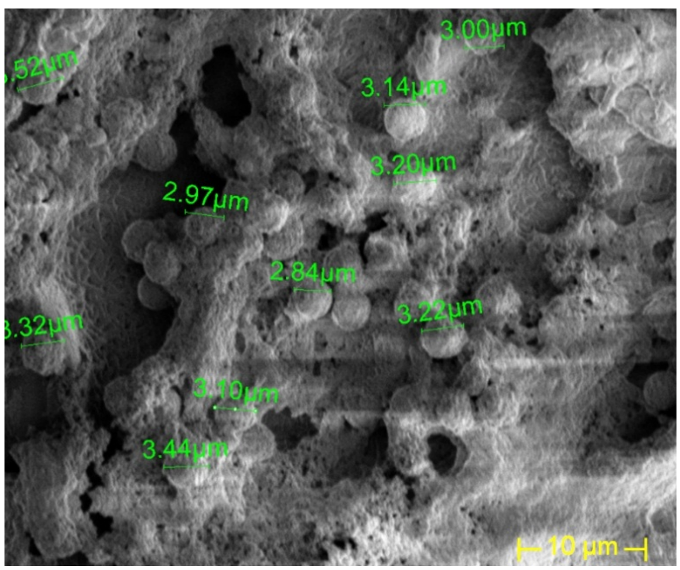

Fig. S3 SEM of magnetic composite on Toray paper at 6000x magnification and1 keV; charging evident at this magnification

Electrochemical Evaluation

All electrochemical procedures, including electrodeposition of the Ni^{2+} and cyclic voltammetry were conducted in a standard three-electrode setup, with a platinum mesh counter electrode and a Ag|AgCl reference electrode. The working electrodes here are Toray paper electrodes that have been wax coated to expose 1 cm^2 of geometric working electrode area. Instrumentation includes a CH Instruments 650 C potentiostat with multiplexer or a Digi-Ivy 2300 bipotentiostat.

Control cyclic voltammograms: Cyclic voltammetry (CV) was conducted on Toray paper electrodes without electrodeposited Ni^{2+}. These electrodes act as controls for the effects of composite casting on Toray paper and indeed show that no additional catalysis is occurring due to either the TBAB modified Nafion films or the magnetic composites. Indeed, the microparticles show decreased capacitance in the 0.1 M NaOH (Figure S4), 1 M methanol (Figure S5), and 0.5 M n-butanol solutions (Figure S6). Additionally, the voltammetry shows that both the TBAB modified Nafion and the magnetic composite are electrochemically inert. There is no statistical difference between the current density of the TBAB modified Nafion electrode and the magnetic composite modified electrodes at 0.8V vs. Ag|AgCl in 0.1M NaOH, but there is a decrease in current response due to the magnetic composite for both fuels.

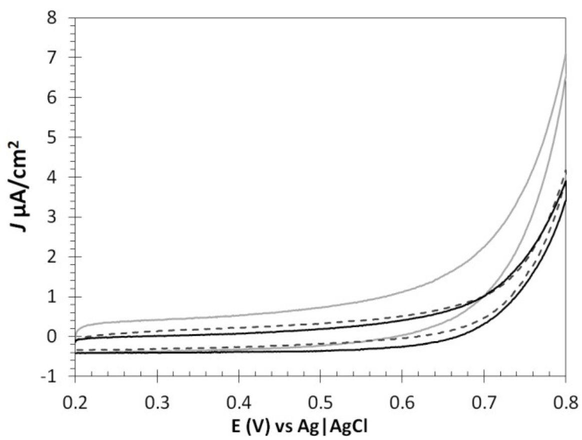

Fig. S4 Representative cyclic voltammograms of Toray paper electrodes in 0.1 M NaOH solution: Toray paper control in light gray (solid), TBAB modified Nafion coated Toray paper in medium gray (dashed), and magnetic composite in dark gray (solid), stable current response after three cycles at scan rate = 50mV/sec.

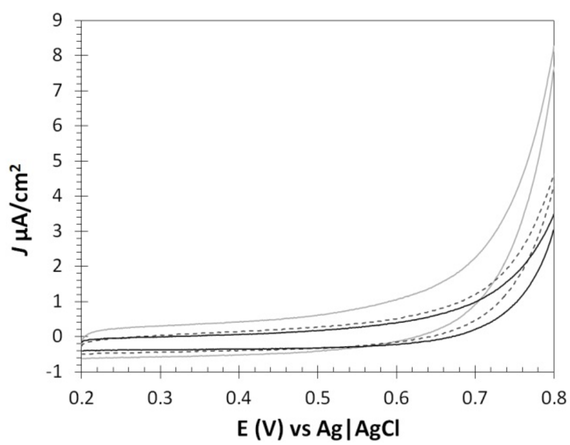

Fig. S5 Representative cyclic voltammograms of Toray paper electrodes in 0.1 M NaOH / 1 M methanol solution: Toray paper control in light gray (solid), TBAB modified Nafion coated Toray paper in medium gray (dashed), and magnetic composite in dark gray (solid), stable current response after three cycles at scan rate = 50mV/sec.

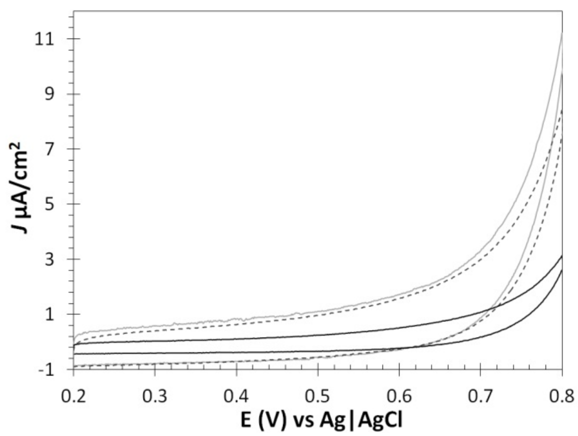

Fig. S6 Representative cyclic voltammograms of Toray paper electrodes in 0.1 M NaOH solutions / 0.5 M n-butanol: Toray paper control in light gray (solid), TBAB modified Nafion coated Toray paper in medium gray (dashed), and magnetic composite in dark gray (solid), stable current response after three cycles at scan rate = 50mV/sec.

Current Response as a Function of Sweep Number: Cyclic voltammetry was performed to understand the current response with sweep number. Current response as a function of sweep number increases throughout the first cycles. After approximately 10 cycles, the response reaches steady state, as shown in Figure S7. The responses of Ni^{2+} Toray paper electrodes with composite films in 0.1 M NaOH, 1 M methanol, and 0.5 M n-butanol are given below in Figure S8, S9, and S10.

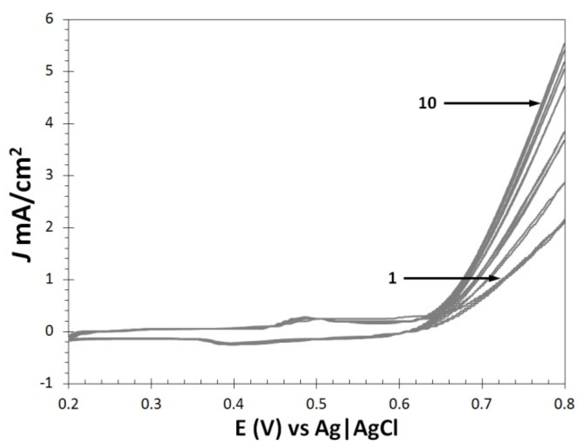

Fig. S7 Representative cyclic voltammetry of growing-in current response as a function of sweep number with Ni modified Toray paper.

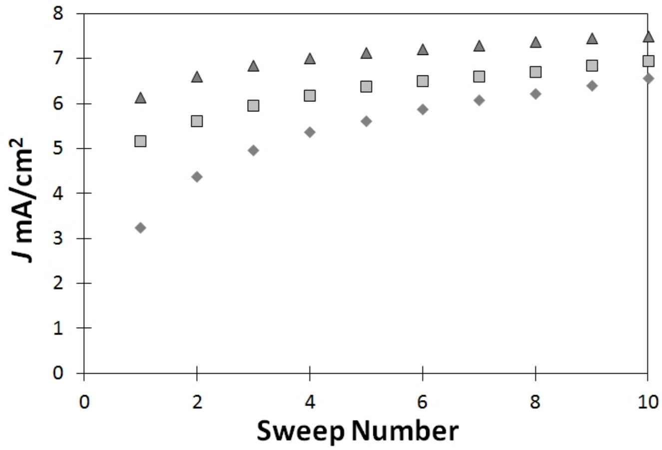

Fig. S8 Average current response as a function of sweep number in 0.1 M NaOH solution for Ni^{2+} deposited Toray paper (diamonds), TBAB modified Nafion coated Ni deposited Toray paper electrodes (squares), and magnetic composite coated Ni deposited Toray paper electrodes (triangles)

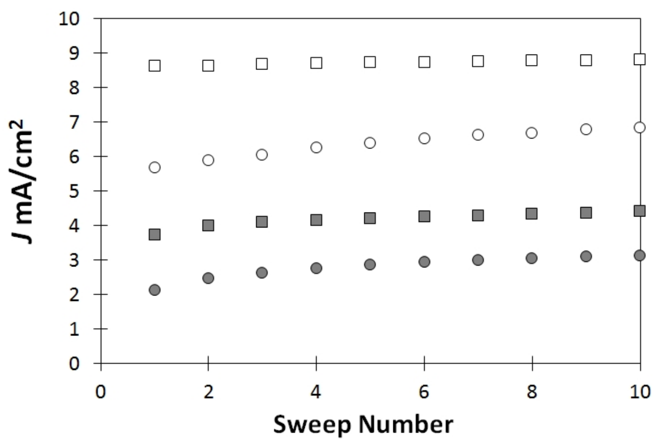

Fig. S9 Average current response as a function of sweep number in 0.1 M NaOH / 1 M methanol solution for: TBAB modified Nafion coated Ni catalyst electrodes at 0.8 V (gray circle), TBAB Nafion composite electrodes at 0.65 V (white circle), magnetic Nafion composite electrodes at 0.8 V(gray square), and magnetic Nafion composite electrodes at 0.7 V (white square)

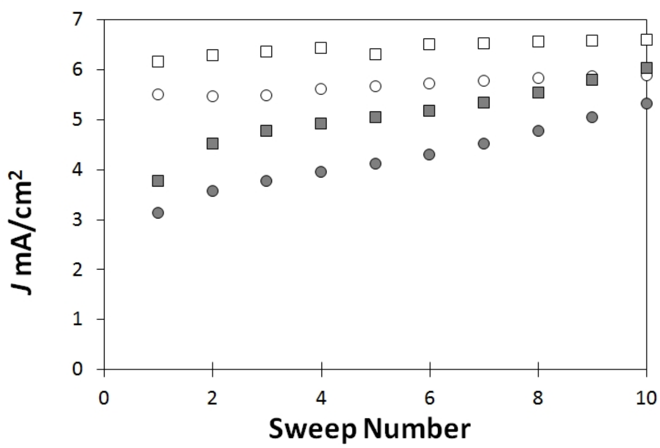

Fig. S10 Average current response as a function of sweep number in 0.1 M NaOH / 0.5 M n-butanol solution for: TBAB Nafion composite electrodes at 0.8 V (gray circle), TBAB Nafion composite electrodes at 0.65 V (white circle), magnetic Nafion composite electrodes at 0.8 V (gray square), and magnetic Nafion composite electrodes at 0.7 V (white square)

References

1. Klotzbach, T.; Watt, M.; Anasari, Y.; Minteer, S. D., *J. Membrane Science* 2006, *282*, 276-283.