



Short communication

## Electro-oxidation of $\text{BH}_4^-$ in dimethylsulfoxide and dimethylformamide studied by rotating disk electrode voltammetry

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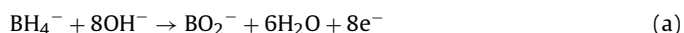
## ABSTRACT

Borohydride ( $\text{BH}_4^-$ ) is a promising new fuel for fuel cells, yet its practical implementation has been hindered by a deleterious hydrolysis reaction to form  $\text{H}_2$  in aqueous solvents, especially at the high  $\text{BH}_4^-$  concentrations necessary for high-power fuel cells. We investigated a wide array of nonaqueous solvents for their ability to hold  $\text{BH}_4^-$  at higher concentrations and allow effective electro-oxidation at Pt and Au, two well-studied  $\text{BH}_4^-$  anode materials. Only dimethylsulfoxide and dimethylformamide were found to be suitable, and precluded  $\text{BH}_4^-$  decomposition to  $\text{H}_2$  in bulk solution (hydrolytic or otherwise).  $\text{BH}_4^-$  decomposition at electrode surfaces was still observed, however. Current densities in these solvents were about an order of magnitude below those observed in aqueous solution, and onset potentials were 0.7 V less favorable. MeOH addition, to stabilize oxidized states of boron, did not increase current.

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## 1. Introduction

Borohydride ( $\text{BH}_4^-$ ) has attracted intense attention as a high-power fuel, either used directly or indirectly (via hydrolysis to  $\text{H}_2$ ) to generate power in fuel cells [1,2]. The power and energy density available come from its low onset potential ( $-1$  V vs. Ag/AgCl at Pt), fast kinetics for oxidation [3], high aqueous solubility (14.5 M [4]) and diffusion coefficient ( $1.67 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  [5]), and the ability to provide up to  $8e^-$  [6]:



Unfortunately, utilization of direct  $\text{BH}_4^-$  oxidation is plagued by its hydrolysis to  $\text{H}_2$ , which occurs in aqueous solution, especially at low pH, and is also catalyzed at Pt surfaces [7]. Hydrolysis can consume up to all  $8e^-$ , although partial hydrolysis to practically any electron count is possible [8]:



Though the hydrolysis can be slowed at high pH, it proceeds even at pH 14 [7], and hydrolysis is first order with  $[\text{BH}_4^-]$  [6,8]. This becomes rather deleterious, as hydrolysis is enhanced at the greater  $[\text{BH}_4^-]$  practical and necessary for to high-power fuel cell development.

The most logical solution to hydrolysis, then, would be to remove water from the system altogether, and operate in a nonaqueous solvent instead. Since facile syntheses for  $\text{BH}_4^-$  compounds were first discovered [9],  $\text{BH}_4^-$  has been employed a reducing agent for many organic syntheses, and, as such, has been used in a variety of nonaqueous solvents [10]. However,  $\text{BH}_4^-$  solutions were not always stable in these studies; even if  $\text{BH}_4^-$  made only a suspension, or decomposed in the solvent, it could still perform the reaction, and the total utilization efficiency of  $\text{BH}_4^-$  was not always the highest priority.  $\text{NaBH}_4$  was found to be soluble in both MeOH and EtOH, but unfortunately decomposed to  $\text{H}_2$  in both. The methanolysis reaction was rapid, whereas the ethanolysis was much slower [11,12]. As with the hydrolysis, the methanolysis was first order with respect to  $[\text{BH}_4^-]$  [11].  $\text{NaBH}_4$  has been shown to form a suspension in tetrahydrofuran (THF) [13], *i*-PrOH, and *t*-BuOH [14]. Brown et al. observed that solutions/suspensions of  $\text{NaBH}_4$  in *i*-PrOH, diethylene glycol dimethyl ether (diglyme) and triglyme did not undergo  $\text{BH}_4^-$  decomposition to  $\text{H}_2$  [15], though Lalancette et al. observed  $\text{H}_2$  formation when making sulfurated borohydrides in THF, diglyme, and other solvents [16,17]. Other  $\text{BH}_4^-$  reactions have been carried out in ether [18], dioxane [12,19], ethyl ether, isopropyl ether, hexamethyl phosphoric triamide, diethylamine, triethylamine, carbon disulfide, dimethylsulfoxide (DMSO), benzene, and various other alcohols and ketones [16]. Sigma-Aldrich® currently sells solutions of  $\text{NaBH}_4$  in diglyme (0.5 M), triglyme (2.0 M), and tetraglyme (3 M).

As will be discussed below, we found great difficulty in obtaining expected current densities from  $\text{BH}_4^-$  in several of these solvents, and we speculated that  $\text{BH}_4^-$ 's fully oxidized form,  $\text{BO}_2^-$  or  $\text{B}(\text{OH})_4^-$

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[3], may not easily form in solvents without a ready supply of oxy-ions, preventing the full  $8e^-$  from being obtained. If this is the case, the stability and ease of formation of boron's solvation shell may be critical to determining current efficiency in a nonaqueous  $BH_4^-$  fuel cell. Previously, it was observed that  $BH_4^-$  is oxidized to  $B(OCH_3)_4^-$  in MeOH [11,13,20], and that  $BH_4^-$ 's reducing activity was influenced by the type of alcohol present to act as a ligand to its oxidized form [20]. Thus we also attempted adding small amounts of MeOH to the system, with the goal of facilitating formation of the fully oxidized  $B(OCH_3)_4^-$  complexes.

## 2. Experimental methods

### 2.1. Reagents and solutions

All chemicals used were reagent grade, and included sodium borohydride ( $NaBH_4$ ), 98%, potassium borohydride ( $KBH_4$ ), 97%, high-purity sulfuric acid, 99.999%, tetrabutylammonium hexafluorophosphate (TBAH), 98%, dimethylformamide (DMF), 99.8%, acetonitrile, 99.8% (Sigma Aldrich), sodium nitrate ( $NaNO_3$ ), dimethylsulfoxide (DMSO), 99.9%, methanol, 99.9%, isopropanol, 99.5%, tetrahydrofuran, 99% (Mallinckrodt), ether, 99.9%, 1-propanol (Fisher), diglyme, 99.0% (Fluka), ethanol (Pharmco-Aaper).

Electrode cleaning solutions were prepared with deionized water purified with a Barnstead Nanopure Analytical UV system (18 M $\Omega$  cm). Organic solutions were used in open-air, without concern for solvent hydration. Electrolyte choice was based on simplicity and previous experience.  $NaNO_3$  is a simple inorganic compound and worked well with DMSO, while DMF would not dissolve various perchlorate salts to 0.1 M, and instead required TBAH.  $Li^+$  and  $Na^+$  salts are inherently more soluble in most solvents than  $K^+$  salts, and  $LiBH_4$  is currently about ten times the price of  $NaBH_4$  without offering a comparable gain in solubility, so  $NaBH_4$  was selected for  $BH_4^-$  solubility assessment.  $NaBH_4$  is hygroscopic and reacts with water, tending to decompose in air slowly over time.  $KBH_4$  is non-hygroscopic [21], and so was chosen for the analytical electrochemistry. Both sodium and potassium borohydride were stored in a desiccator to minimize any possible decomposition prior to experimentation.

### 2.2. Electrochemical setup and electrode cleaning

Experiments were carried out in a three-chambered electrochemical cell, with compartments separated by medium porosity glass frits, using a Pt-mesh counter electrode and a Pt/PtO pseudoreference. The potential of the Pt/PtO pseudoreference was measured against an Ag/AgCl reference electrode in the corresponding solvent immediately prior to experimentation, and all potentials are referenced vs. Ag/AgCl. Rotating disk electrode voltammetry was performed using a Pine bipotentiostat (Model AFCBP1) and analytical rotor (Model AFMSRX). Electrodes were rotated between 50 and 3000 rpm. CV's were swept at 20 mV  $s^{-1}$  to obtain pseudo steady-state sweeps. All experiments were run at room temperature and pressure (25 °C, 1 atm). The 3 mm Pt rotating disk electrode was polished using 1  $\mu$ m diamond paste (Buehler Metadi) on a polishing cloth (Buehler Microcloth). The Pt electrode was then electrochemically cleaned from  $-0.2$  to  $+1.2$  V vs. Ag/AgCl in 0.1 M  $H_2SO_4$  until the characteristic voltammetric profile of polycrystalline Pt was obtained. The 5 mm Au rotating disk electrode was polished using a series of 1 and 0.3  $\mu$ m  $\alpha$ -alumina and 0.05  $\mu$ m  $\gamma$ -alumina polishes (Buehler Micropolish). The Au electrode was then electrochemically cleaned from 0.0 to  $+1.35$  V vs. Ag/AgCl in 0.1 M  $H_2SO_4$  until the characteristic voltammetric profile of polycrystalline Au was obtained.

### 2.3. Electrochemical analysis

In rotating disk electrode (RDE) voltammetry, the number of electrons involved in an oxidation reaction at a chosen potential can be obtained from the Levich equation (Eq. (1)) [22]:

$$i_{l,a} = -0.62nFAD_R^{2/3}\omega^{1/2}\nu^{-1/6}C_R^* \quad (1)$$

where  $i_{l,a}$  is the limiting anodic current at a given rotation rate ( $\omega$ ),  $n$  is the number of  $e^-$  transferred,  $F$  is Faraday's constant,  $A$  is the electrode area ( $cm^2$ ),  $D_R$  is the diffusion coefficient of the reduced species ( $cm^2 s^{-1}$ ),  $\omega$  is the electrode rotation rate ( $rad s^{-1}$ ),  $\nu$  is the kinematic solution viscosity ( $cm^2 s^{-1}$ ), with  $\nu = \mu/\rho$  (where  $\mu$  is the solution viscosity, g (cm s) $^{-1}$ , and  $\rho$  is the solution density, g  $cm^{-3}$ ), and  $C_R^*$  is the bulk concentration of the reduced species (mol  $cm^{-3}$ ). For our analyses of  $BH_4^-$ , we have used the diffusion coefficient for  $BH_4^-$  determined by Denuault et al.,  $1.67 \times 10^{-5} cm^2 s^{-1}$  [5]. The kinematic viscosities of DMSO solutions were based on standard values for DMSO's viscosity and density: 1.99 mPa and 1.10 g  $cm^{-3}$ , respectively [4]. Small deviances due to addition of electrolyte or analyte were neglected, as they are practically eliminated by the  $-1/6$  power for  $\nu$ . The Levich equation is valid when the system is mass-transport limited at all rotation rates used in the calculation, and this is evidenced by linearity in the Levich plot ( $i_{l,a}$  vs.  $\omega^{1/2}$ ).

In this study, both  $n$  and  $D_R$  appeared conspicuously low, and are speculated upon in Section 3. Since  $D_R$  is significantly below a common literature value [5], the exact value of  $n$  could not be readily obtained, and evaluation of kinetic parameters was not performed. Though techniques do exist to simultaneously determine  $n$  and  $D$  [5,23], the results obtained herein were not promising enough to justify a more extensive analysis.

## 3. Results and discussion

### 3.1. Solvent selection for $BH_4^-$

The criteria for selection of a nonaqueous solvent for  $BH_4^-$  were based on improving past fuel cell results. Our previous work showed exceptional oxidation performance for  $BH_4^-$  in basic aqueous solutions, with nearly all  $8e^-$  recovered at the expected  $D_R$  of  $1.67 \times 10^{-5} cm^2 s^{-1}$ , and, for Pt, with fast kinetics as well [3]. However, since  $BH_4^-$  decomposes to  $H_2$  at higher concentrations, excessive base was needed to stabilize solutions of  $BH_4^-$  [6,8]. The [NaOH] was limited to about 3 M, with higher concentrations resulting in degradation of various fuel cell components. This in turn limited our [ $BH_4^-$ ] to approximately 0.15 M [24]. To represent a significant improvement from our current system, we decided that  $BH_4^-$  must be soluble to  $>0.4$  M in a nonaqueous solvent, and that the new  $BH_4^-$  solution must not have any new problematic side effects that would diminish and/or compromise system performance.

$NaBH_4$ 's solubility was tested in many solvents with a wide range of polarity (Table 1; see Section 2 for use of  $NaBH_4$  vs.  $LiBH_4$  and  $KBH_4$ ). We limited the scope of this study by choosing mostly polar, common solvents, and we expect that our results can help predict  $NaBH_4$ 's relative solubility in many solvents not included in our analysis. This assessment of solubility was intentionally coarse and the solubilities should be treated as semi-quantitative only. The results are obtained from simple room-temperature experiments, without heating. Complications were closely monitored and are likewise noted with the solubilities.

Many of the solvents tested did not show any significant solubility for  $NaBH_4$  at all, and of those that did, most had significant drawbacks for use (Table 1). As expected,  $BH_4^-$  decomposed to  $H_2$  bubbles in both MeOH and EtOH, but the reactions occurred at surprisingly fast rates, precluding both solvents from practical utility.

**Table 1**

Solubility of  $\text{NaBH}_4$  in a variety of nonaqueous, mostly polar solvents, and complications regarding the stability of each solution.

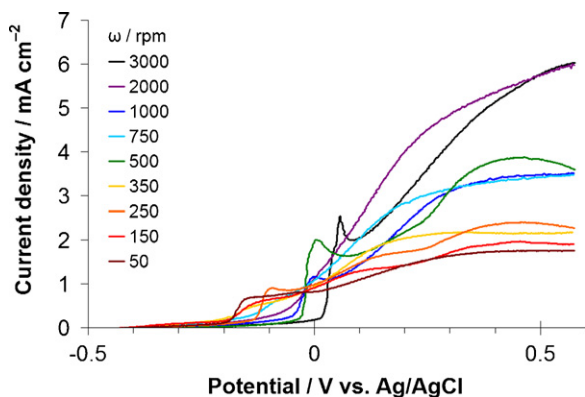
Solvent	$\text{BH}_4^-$ Solubility at 25 °C (M)	Complications
DMSO	0.42	
DMF	0.43	
Acetonitrile	–	Not soluble
Diglyme	0.46	Suspension
Ether	–	Not soluble
Methanol	0.33	Bubbles
Ethanol	0.49	Bubbles
Isopropanol	–	Not soluble
1-Propanol	–	Not soluble
THF	–	Not soluble

Considering the various high-concentration glyme solutions available from Sigma–Aldrich®, diglyme was rather disappointing, as the saturated solution was very cloudy, indicating that a suspension formed to some degree. Out of a fairly wide pool of solvents, we quickly narrowed our focus down to DMF and DMSO, and chose appropriate electrolytes for each (see Section 2).

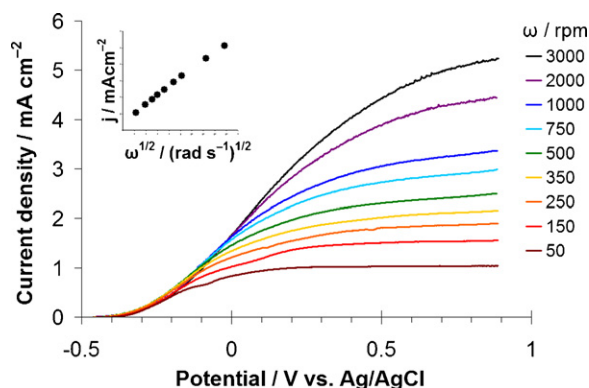
### 3.2. $\text{BH}_4^-$ oxidation in DMF and DMSO

Both of our selected solvents proved very challenging to work with. The RDE voltammograms for  $\text{BH}_4^-$  oxidation often did not show standard shape or have well-defined mass-transport limited regions [22] in these solvents. Early trials were poorly reproducible (see Supporting Information, Fig. S1). Studies at Pt in DMF often showed decreased current on later scans, indicating slow poisoning reactions (Fig. S2). In fact, we were never able to get a clean voltammogram with DMF (Fig. 1), preventing a more thorough quantitative analysis.

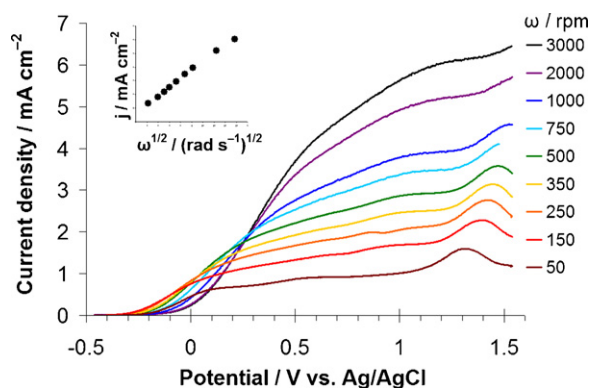
Though early trials of  $\text{BH}_4^-$  in DMSO resembled those in DMF (Fig. S3), we were eventually able to obtain much cleaner voltammograms at Pt (Fig. 2) by finding a more appropriate solvent window (–0.5 to +0.9 V vs. Ag/AgCl), which prevented reactions with the solvent from interfering with the current from  $\text{BH}_4^-$  oxidation. Some degree of a linear, probably resistive trend was still evident in the mass-transport-limited region of the voltammograms, but a highly linear Levich plot was nonetheless obtained (Fig. 2, inset). The same experiment performed at Au produced  $i_L$ 's about 20% higher, though the additional current was available only at higher potentials, kinetics were slower, and onset potentials were more positive (Fig. 3). The Au voltammograms were somewhat more prone to solvent poisoning in the wider potential window used (–0.5 to +1.5 V vs. Ag/AgCl), as evidenced by increases in onset potential with time (seen here as later rotation rates, e.g. 2000 and 3000 rpm).



**Fig. 1.** RDE voltammogram anodic sweeps of 5 mM  $\text{KBH}_4$  in DMF, 0.1 M TBAH, at a Pt disk electrode,  $20 \text{ mV s}^{-1}$ , rotated between 50 and 3000 rpm.



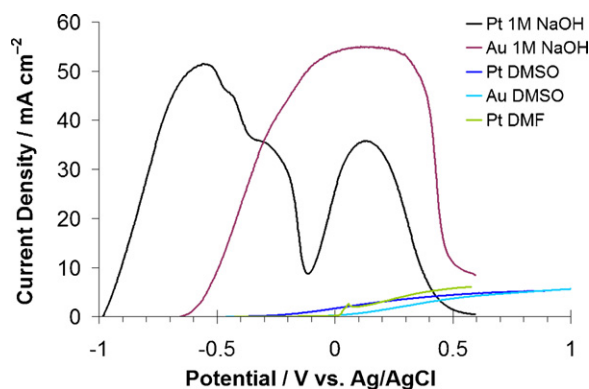
**Fig. 2.** RDE voltammogram anodic sweeps of 5 mM  $\text{KBH}_4$  in DMSO, 0.1 M  $\text{NaNO}_3$ , at a Pt disk electrode,  $20 \text{ mV s}^{-1}$ , rotated between 50 and 3000 rpm. Inset: Levich plot sampled at  $E = +0.8 \text{ V}$ .



**Fig. 3.** RDE voltammogram anodic sweeps of 5 mM  $\text{KBH}_4$  in DMSO, 0.1 M  $\text{NaNO}_3$ , at an Au disk electrode,  $20 \text{ mV s}^{-1}$ , rotated between 50 and 3000 rpm. Inset: Levich plot sampled at  $E = +1.2 \text{ V}$ .

These observed currents, however, were well below expectation. Our previous study of  $\text{BH}_4^-$  oxidation in 1 M NaOH (base) at Pt and Au produced current densities above  $50 \text{ mA cm}^{-2}$  [3] while those observed in this investigation are approximately 10 times lower (Fig. 4), and occur at potentials 0.2–0.5 V more positive (less favorable). These initial results suggest that DMSO and DMF significantly diminish fuel cell power obtainable from  $\text{BH}_4^-$  oxidation.

As many terms in the Levich equation were standard between base and DMSO, the decrease in current must be due to changes in either  $n$ ,  $D_R$ , or  $\nu$ . The change in  $\nu$  is fairly insignificant; though



**Fig. 4.** Comparison of  $\text{BH}_4^-$  oxidation at Pt and Au in 1 M  $\text{NaOH}_{(\text{aq})}$  (5 mM  $\text{NaBH}_4$ ,  $25 \text{ mV s}^{-1}$ ), in DMSO with 0.1 M  $\text{NaNO}_3$ , and in DMF with 0.1 M TBAH (5 mM  $\text{KBH}_4$ ,  $20 \text{ mV s}^{-1}$ ). RDE voltammogram anodic sweeps are shown at 3000 rpm, anodic sweeps only.



$\nu_{1\text{ M NaOH}} = 1.2 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$  and  $\nu_{\text{DMSO}} = 1.8 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$  (inferred from various tables in Lide [4]), these values are raised to the  $-1/6$  power in the Levich equation (see Section 2), making the terms in the final expression nearly identical. The current decrease must then be due to either  $D_R$  or  $n$ , implying either a change in solvent interaction or reaction mechanism, respectively. Typically,  $D$  has minimal variance from  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , even across wide ranges of polarity of solute [4], and by extension, polarity of solvent. If  $n$  dropped from 8 [3] to only  $1e^-$ ,  $D_R$  would have had to decrease by 40% from  $1.7 \times 10^{-5}$  to  $1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . Since  $n < 1$  is rather unlikely,<sup>2</sup> and  $n > 1$  implies an even larger decrease in  $D_R$ , it can be concluded that  $\text{BH}_4^-$  had weaker solvent interaction in DMSO than in base. Since  $D_R < 5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  would be required for  $n=8$ , which represents an essentially unphysically small value for  $D_R$ , it is clear that  $n$  for  $\text{BH}_4^-$  oxidation is lower in DMSO than in base, suggesting that DMSO mechanistically hinders the  $\text{BH}_4^-$  oxidation pathway. There do exist procedures to determine  $n$  and  $D_R$  simultaneously when given  $C_R^*$ , such as comparison of transient and steady-state responses from an ultramicroelectrode [5], or comparison of the slope and intercept from hydrodynamic chronocoulometry [23]. Given that the results obtained suggest that DMSO is not an ideal solvent for  $\text{BH}_4^-$  fuel cells, we did not feel that further analysis would yield actionable information, and these techniques were not attempted.

Our cursory analysis of  $n$  and  $D$  does suggest, however, that  $\text{BH}_4^-$ 's  $n$  in DMSO is probably very small, and improvement of  $\text{BH}_4^-$ 's oxidation mechanism in DMSO could yield significantly higher current densities. As described in the Introduction, previous studies found that  $\text{BH}_4^-$  coordinated methoxy groups during its oxidation, and the nature of such alcohol-derived ligands influenced  $\text{BH}_4^-$ 's reactivity. We hypothesized that, because  $\text{BH}_4^-$  had a comparatively weak solvent interaction with DMSO, it may not coordinate DMSO effectively in its oxidized state. Thus, availability of MeOH to promote formation of the fully oxidized form  $\text{B}(\text{OCH}_3)_4^-$  could result in a higher  $n$  and therefore increased current from  $\text{BH}_4^-$ 's oxidation.

### 3.3. Effect of MeOH on $\text{BH}_4^-$ oxidation in DMSO

To examine the effect of adding MeOH to the system, we first assessed whether MeOH would produce its own current, serving as a second fuel in solution. No significant current was obtained from MeOH oxidation in the absence of  $\text{BH}_4^-$  within the potential range studied (Fig. S4). Any current increase from MeOH addition was therefore due to enhanced  $\text{BH}_4^-$  oxidation only.

Addition of equimolar (5 mM) MeOH at first appeared to increase  $\text{BH}_4^-$ 's limiting current density by about 10% (from 5.2 to  $5.7 \text{ mA cm}^{-2}$  in Figs. 2 and 5, respectively). Since MeOH appeared to boost current, perhaps by serving as a single coordinating ligand, we then tried adding MeOH in a 4:1 molar ratio with  $\text{BH}_4^-$  to allow formation of the four-coordinate species,  $\text{B}(\text{OCH}_3)_4^-$ . In case MeOH had low activity in DMSO, we added 50% extra MeOH (30 instead of 20 mM), to ensure saturation of any current-boosting effect from coordination. Instead of further increasing current, 30 mM MeOH actually decreased currents to their original levels (Fig. 6). Considering that we had a small degree of variance in currents across multiple trials, it is likely that the current increase observed with 5 mM MeOH falls within experimental error, and that MeOH addition has no significant effect on  $\text{BH}_4^-$  oxidation in DMSO. The trials with and without MeOH that are most similar are shown in Fig. 7.

<sup>2</sup> The most probable case for  $n < 1$  would be dimer formation ( $n=0.5$ ), but this would require  $D=3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , which is physically very unlikely.

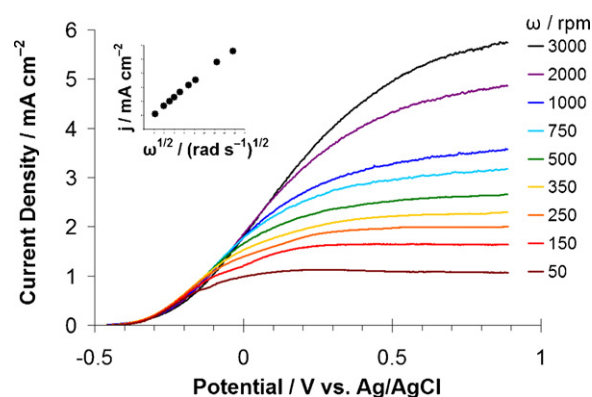


Fig. 5. RDE voltammogram anodic sweeps of 5 mM  $\text{KBH}_4$  with 5 mM MeOH in DMSO, 0.1 M  $\text{NaNO}_3$ , at a Pt disk electrode,  $20 \text{ mV s}^{-1}$ , rotated between 50 and 3000 rpm. Inset: Levich plot sampled at  $E = +0.8 \text{ V}$ .

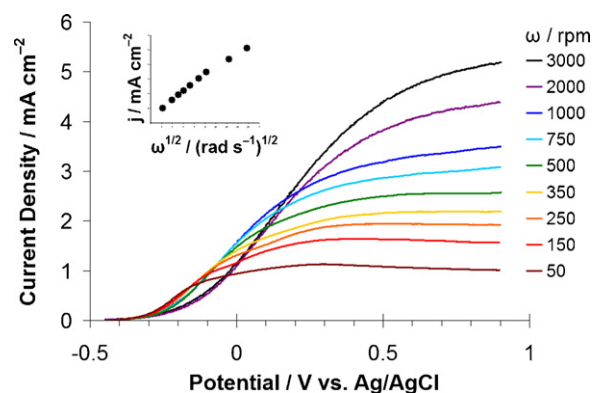


Fig. 6. RDE voltammogram anodic sweeps of 5 mM  $\text{KBH}_4$  with 30 mM MeOH in DMSO, 0.1 M  $\text{NaNO}_3$ , at a Pt disk electrode,  $20 \text{ mV s}^{-1}$ , rotated between 50 and 3000 rpm. Inset: Levich plot sampled at  $E = +0.85 \text{ V}$ .

### 3.4. Solvent effects on $\text{BH}_4^-$ hydrolysis, electron recovery, and diffusivity

Although we were unable to increase  $\text{BH}_4^-$ 's oxidative current in DMSO to levels seen in base, both DMSO and DMF were able to successfully dissolve large quantities of  $\text{NaBH}_4$  without permitting homogeneous or passive heterogeneous  $\text{BH}_4^-$  hydrolysis. No bubbles were evident during solubility tests, with  $[\text{BH}_4^-] > 0.4 \text{ M}$ , nor at electrode surfaces in 5 mM  $\text{BH}_4^-$  solutions at open circuit. In contrast, basic solutions of just 5 mM  $\text{BH}_4^-$  will quickly and visibly

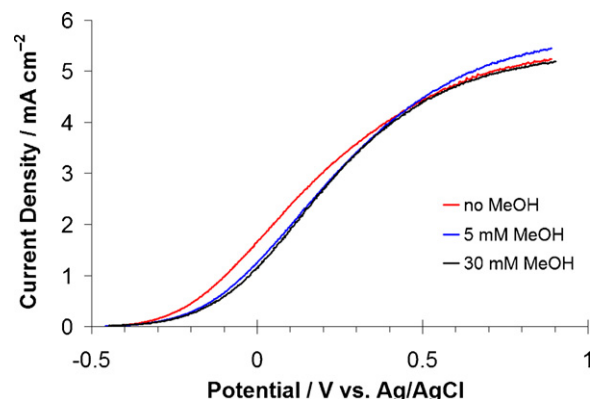


Fig. 7. Comparison of RDE voltammogram anodic sweeps of 5 mM  $\text{KBH}_4$  in DMSO, 0.1 M  $\text{NaNO}_3$ , at a Pt disk electrode,  $20 \text{ mV s}^{-1}$ , rotated at 3000 rpm, with 0, 5, and 30 mM MeOH added.

(via bubbles) be hydrolyzed at Pt oxide at open circuit. Unfortunately, we noticed that heterogeneous hydrolysis at both Pt and Au still occurred vigorously upon oxidative current discharge, with bubbles quickly covering the electrode surfaces. Thus, even in an environment with minimal  $[H_2O]$ ,  $BH_4^-$  either reacts with trace amounts of  $H_2O$  or uses its own H atoms to produce to  $H_2$ .

It is unclear why Au was able to produce a larger  $i_l$  for  $BH_4^-$  oxidation in DMSO than Pt (Figs. 2 and 3). This would imply that  $n$  was 20% larger in  $BH_4^-$ 's oxidation mechanism at Au vs. Pt. This sort of proportionality would best be explained by an increase in  $n$  from 5 to 6, but the corresponding  $D_R$  would be  $1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , which is exceptionally small. Given that Au can significantly improve  $n$ , perhaps other catalysts will increase the available current from  $BH_4^-$  in nonaqueous solvents. It would be nontrivial, however, to find a catalyst that could improve current densities by 10 times to reach existing current densities in base. Furthermore, a low value for  $D_R$  would strictly limit  $i_l$  regardless of the catalyst employed, and suggest that the first step to improving current would be finding a more suitable solvent.

#### 4. Conclusions

The nonaqueous solvents DMSO and DMF were found to provide a fuel cell environment that helped mitigate, but did not eliminate, complications arising from  $BH_4^-$ 's catalytic decomposition to  $H_2$ . Though homogeneous and passive heterogeneous decomposition were prevented, Pt and Au both produced  $H_2$  from  $BH_4^-$  upon passage of current, as they do in basic, aqueous solutions.

Using nonaqueous solvents for electrochemical reactions at noble metals is inherently challenging. Both DMSO and DMF interacted with Pt and Au surfaces, resulting in unexpected poisoning and side reactions, which limited the electrical potential window in which they could operate. DMF was unable to support a reproducible oxidation of  $BH_4^-$  under any of the conditions studied. Additionally, there may exist complications in achieving high conductivity in DMSO [25] and DMF [26], although further discussion lies outside the scope of this investigation. While highly concentrated mixtures of  $NaBH_4$  can be prepared in various glymes,  $NaBH_4$  – saturated diglyme appeared to be a suspension, rather than a solution, and would not be expected to be a good medium for heterogeneous catalysis. Thus solutions that work well for synthetic organic chemistry will not necessarily yield facile solvent systems for heterogeneous, electrochemical reactions.

The oxidations of  $BH_4^-$  in DMSO and DMF were found to produce ten times less current and 0.7 V less voltage than in 1 M NaOH, indicating that DMSO and DMF are not ideal solvents for  $BH_4^-$  fuel cells. The exceptionally low current observed is due to decreases in both  $n$  and  $D_R$  for  $BH_4^-$  oxidation. Current densities in DMSO were about 20% higher at Au than at Pt, suggesting that  $BH_4^-$  undergoes a more complete oxidation at Au in this solvent. Though literature suggested that MeOH could provide methoxy ligands to stabilize

$BH_4^-$ 's oxidized state and affect its reactivity, addition of MeOH was not observed to increase the current obtained from  $BH_4^-$ .

The results herein demonstrate that neither DMSO nor DMF will completely solve complications in  $BH_4^-$  fuel cells arising from  $BH_4^-$ 's decomposition to  $H_2$ . Future solutions may involve finding better solvents that decrease hydrolysis but do not impact  $n$  or  $D_R$ , developing aqueous additives that stabilize  $BH_4^-$ , or implementing engineering solutions that allow unmitigated fuel cell operation irrespective of copious bubble formation.

#### Acknowledgments

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2011.03.034.

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