

Study of NH_3BH_3 electrooxidation reaction on gold electrodes by *in situ* Fourier Transform InfraRed Spectroscopy and on-line Differential Electrochemical Mass Spectrometry

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Introduction

Ammonia borane (NH_3BH_3) electrooxidation reaction (ABOR) was studied on gold electrodes using rotating disk electrode (RDE) and coupled physical techniques: on-line Differential Electrochemical Mass Spectrometry (DEMS) and *in situ* Fourier Transform Infrared Spectroscopy (FTIR).

Results and discussion

Detection of molecular H_2 using DEMS asserted non-negligible AB heterogeneous hydrolysis in the low-potential region (Fig. 1). Gold being not capable of oxidizing H_2 [1], the number of electron exchanged per BH_3OH^- species is *ca.* 3 at low potential; it only reaches *ca.* 6 above 0.6 V vs. RHE. These figures correspond to literature data [1, 2]; they were confirmed by Levich and Koutecki-Levich calculations from ABOR characterisations on a gold disk RDE.

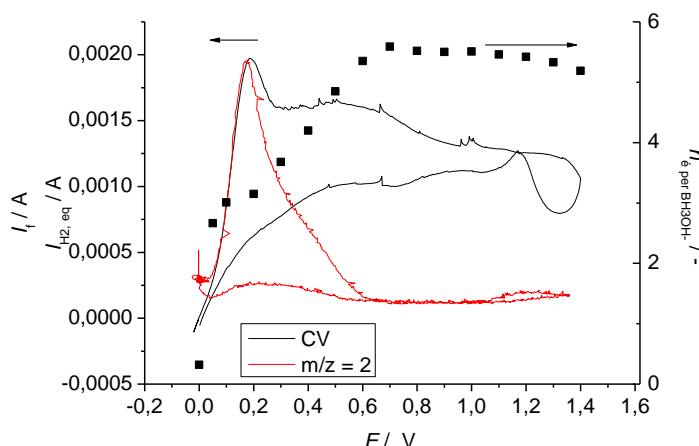
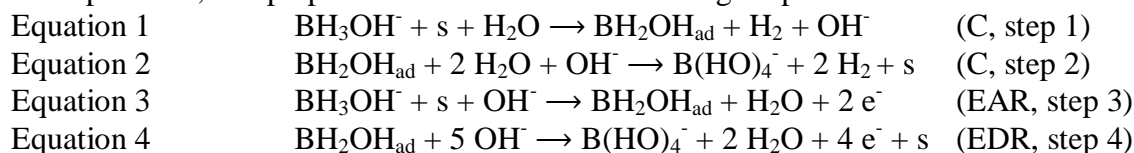


Figure 1. ABOR Faradaic current (I_f) vs. E , resulting equivalent HER current ($|I_{\text{H}_2,\text{eq}}|$) and corresponding variation of n_{e-} per BH_3OH^- . $1 \text{ mol L}^{-1} \text{ NaOH} + 10^{-2} \text{ mol L}^{-1} \text{ NH}_3\text{BH}_3$ solution, RHE reference.

The nature of the ABOR intermediates and products were determined using *in situ* FTIR, as previously attempted for the borohydride electrooxidation reaction (BOR) [3, 4] (Fig. 2). While BH_2 species were detected during the ABOR, their adsorption onto the Au electrode proceeds *via* the O atom, in opposition to what happens during the BOR. Therefore, the mechanism of the ABOR likely differs from that of the BOR. From the whole set of data (RDE, DEMS, FTIR), a relevant reaction pathway was proposed, including competition between the BH_3OH^- heterogeneous hydrolysis (chemical steps (C), Eq. 1 and Eq. 2) and electrooxidation (electrochemical adsorption / desorption reaction, EAR and EDR, Eq. 3 and 4) at low potential, and preponderant electrooxidation at higher potential.



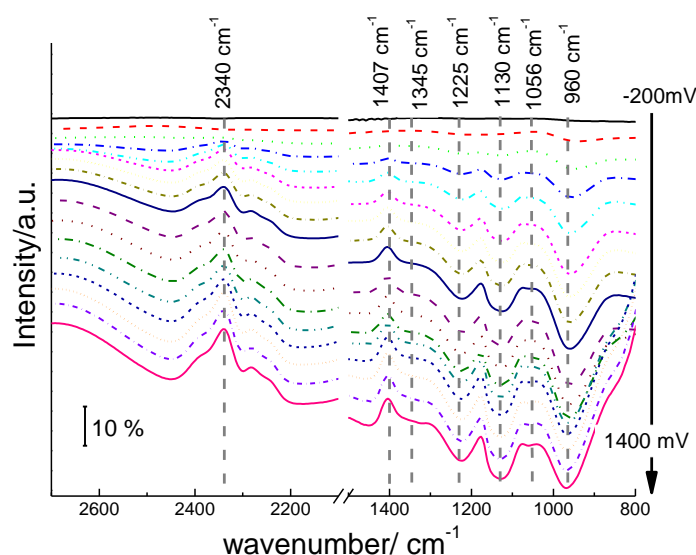


Figure 2. *In situ* infrared spectra recorded on a gold electrode in 1 mol L⁻¹ NaOH + 1 mol L⁻¹ NH₃BH₃ solution for *s*-polarized light; $R_{\text{ref}} = -200$ mV vs. RHE.

Finally, a simplified kinetic modeling accounting with this reaction pathway was proposed, which nicely fits the stationary (*i* vs. *E*) ABOR plot (Fig. 3).

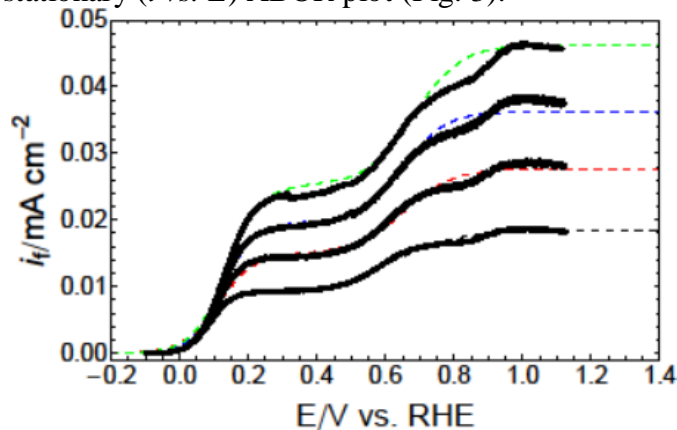


Figure 3. Experimental ABOR CV monitored at 5 mV s⁻¹ on an Au RDE electrode in 10⁻² mol L⁻¹ NH₃BH₃ + 1 mol L⁻¹ NaOH solution at 25°C for various revolution rates of the RDE (bold black line) and corresponding modeled traces (colored dotted lines).

Conclusion

By the *in situ* coupling of physical techniques to electrochemistry and the use of kinetics modeling, the mechanism of NH₃BH₃ oxidation on Au electrodes in alkaline medium was unveiled. The ABOR mechanism differs from that of the BOR because the adsorption of BH_x intermediates generated in the course of the process do not proceed similarly in the two cases.

Acknowledgements

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References

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