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Preliminary Investigation on the Electrochemical Activity of Butanol Isomers as Potential Fuel for Direct Alcohol Fuel Cell

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212-A (Phoenix Convention Center)

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Low molecular weight alcohols have been proposed as promising alternative fuels to H₂ in low temperature fuel cells due to their liquid nature, high energy density, availability in nature and easy handling¹. Methanol and ethanol have been widely studied as fuel for direct alcohol fuel cell (DAFC); however methanol is toxic whereas ethanol is non-toxic and can be produced by fermentation of sugar. However, there is on-going public debate on the ethics of utilizing food stocks for fuel production instead of nutrition². An alternate renewable source, which does not compete with the food, is required for a sustainable long-term energy production. Thus, 2nd generation bio-fuels are produced from non-food based feedstock such as lignocellulose biomass (LCB)²⁻³. Butanol is considered as a 2nd generation bio-fuel with better infrastructure compatibility than ethanol. These C₄ alcohols have higher energy content, lower water adsorption, and better blending ability with gasoline than ethanol and is considered as a promising substitute for gasoline in automobiles²⁻³. In fuel cell, butanol provides 24 electrons on complete oxidation compared to 12e⁻ and 6e⁻ from ethanol and methanol respectively. In this regard, with the recent developments in the bio-butanol production, butanol has the potential to be used as fuel for DAFC. However increasing carbon will increase the number of possible intermediates and complicates the reaction pathway and thus reduces the efficiency.

Within this study, different butanol isomers were examined as potential fuel for DAFC using a three electrode cell set up on Pt and PtSn electrodes prepared by electrodeposition on glassy carbon both in acid and alkaline media. The Sn coverage was calculated from the difference in the hydrogen desorption charge before and after the Sn deposition. A clear difference in behaviour was observed for different butanol isomers in the cyclic voltammetry (CV) indicating their different oxidation activity. N-butanol and iso-butanol showed similar CV features whereas 2-butanol and ter-butanol showed completely different CV features. Ter-butanol was found to be inactive for electrochemical oxidation at room temperature on Pt. Comparing the CV of Pt in butanol and acid, it was clear that the presence of OH_{ads} is necessary to initiate the n-butanol and iso-butanol oxidation on Pt. To enhance this, an oxophilic metal (Sn) was added to Pt so as to initiate the water dissociation at a lower potential. The PtSn electrode showed an improved oxidation activity compared to Pt with a pre-peak at ~500 mV (Figure 1) lower than the onset potential found using Pt for n-butanol oxidation in acidic media. Since this pre-peak appears at a potential region where PtO_x is not formed, the oxygenated species for the butanol oxidation was assumed to be provided by the Sn on the catalyst surface⁴. The higher activity of PtSn was thought to be due to a bi-functional mechanism where the water dissociate on Sn surface to provide OH_{ads} at lower potential which helps in the removal of poisoning species CO from the Pt as CO₂ (equation 1-2). The activation energy calculated at the pre-peak, 0.25 V vs. Ag/AgCl (3M NaCl) for the PtSn was about ~11 kJ mol⁻¹ which is significantly lower than that on pure Pt at the first anodic peak, 0.7 V vs. Ag/AgCl-3M NaCl (25 kJ mol⁻¹). The lower activation energy on PtSn at lower potential could be attributed to their effectiveness in the dissociative adsorption and oxidation of butanol⁵. These results suggests PtSn could be an active catalyst for n-butanol electro oxidation and shows promise for further studies on long chain organic molecules.

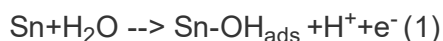
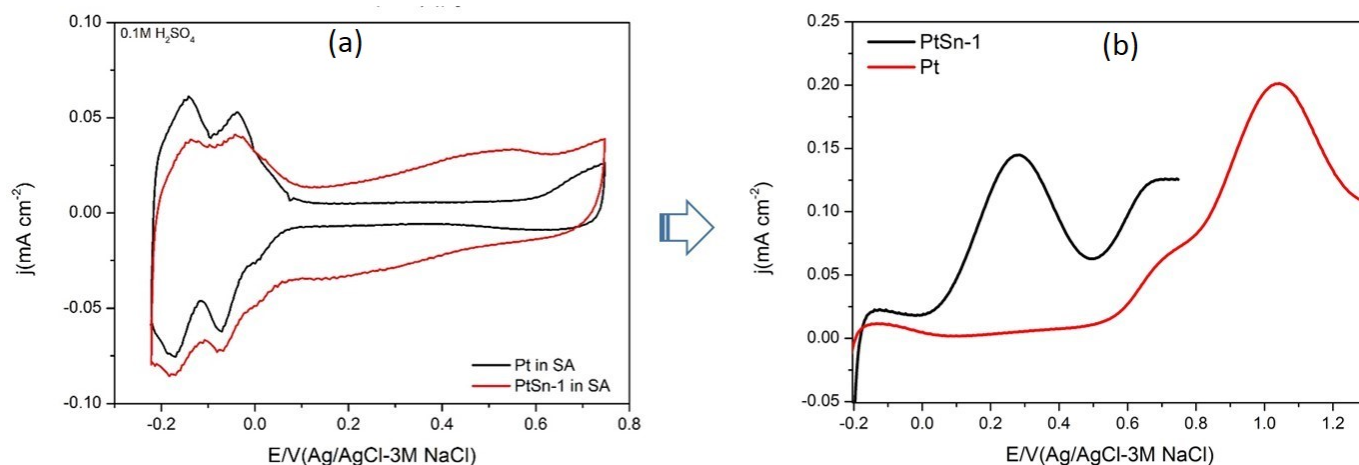


Figure 1. The voltammogram of Pt and PtSn electrodes (a) Pt and PtSn in in 0.1M H₂SO₄ and (b) Pt and PtSn in 0.1M BtOH+0.1M H₂SO₄. Scan rate 50 mVs⁻¹. Sn coverage ~25%.

Reference

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- (4) (a) Gupta, S. S.; Singh, S.; Datta, J. *Materials Chemistry and Physics* **2009**, *116*, 223(b) Beyhan, S.; Coutanceau, C.; Léger, J.-M.; Napporn, T. W.; Kadırgan, F. *International Journal of Hydrogen Energy* **2013**, *38*, 6830.
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