Nanogap Electrochemical Cell for Methanol-Contained Ethanol Solution Detection

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Some alcohol manufacturers had used denatured alcohol as an alternative to produce alcoholic drink, called fake alcoholic drink, for a higher profit, because of the similarities of appearance and odor to edible ethanol as well as the lower manufacturing cost for alcoholic drink. The denatured alcohol, however, contains 5% v/v or more methanol than edible alcohol and is highly toxic to human because the methanol will be metabolized to form formic acid, which is poisonous to human's central nervous system and may cause blindness, coma, and death. [1] Conventionally, the existence of methanol in alcoholic drink is measured by liquid chromatography, spectroscopy, and test paper. The front two methods, nevertheless, are hard to carry in daily life, and the test paper method is only valid in a few months and cannot be tested repeatedly. Therefore, there is a need to conveniently, quickly, and repeatedly test the alcoholic drink in daily life to prevent the methanol poisoning happened.

We recently have applied nanogap electrochemical cells (NECs) as Figure 1 shown, to pure water electrolysis and demonstrated that unlike conventional electrochemical cell, of which electrodes are at a much larger distance, there is a strong electrical field existed between two electrodes in NECs that could improve the ionization of solution and the mass transport rate of ions in solution. [2] The Figure 2 shows the schematic potential distribution in conventional and nanogap cell. Please notice that due to these improvements, no any added electrolyte is required when using NECs for electrolysis, and this is the largest difference between conventional cell and NECs. Due to above advantages, the sensitivity of chemical sensing can be greatly improved and will be a real chemical sensing, no influence from any add electrolytes when utilizing NECs for chemical sensing through electrochemical phenomena.

Nanogap electrochemical cell has been used to conveniently, quickly, and repeatedly detect the content of methanol in water solutions. The electro-oxidations occur at two electrodes as Table 1 shown. [3] The electron transfer at two electrodes can be treated as a current signal for chemical sensing and be used to compare the concentration of methanol in solutions. Due to the stronger chemical bonding, two bonded carbon atoms, of ethanol to methanol, a higher energy for breaking that bonding is required for a completed redox. The NECs can utilize this characteristic to distinguish the methanol and ethanol by differentiating the threshold voltage. The Figure 3 shows the I-V curve of methanol and ethanol in water solutions. From our recent results, our NECs have enough sensitivity to distinguish the content of methanol in the denatured alcohol, and we are optimizing the material composition at anode to further improve the sensitivity to an even lower methanol concentration for the fake alcoholic drink detection.

[1] https://www.thoughtco.com/what-is-denatured-alcohol-p2-603999
[2] Yifei Wang, S. R. Narayanan, and Wei Wu, *ACS Nano*, 2017, 11, (8), 8421–8428
[3] Christophe Coutanceau and Stève Baranton, *WIREs Energy Environ*, 2016, 5:388–400.

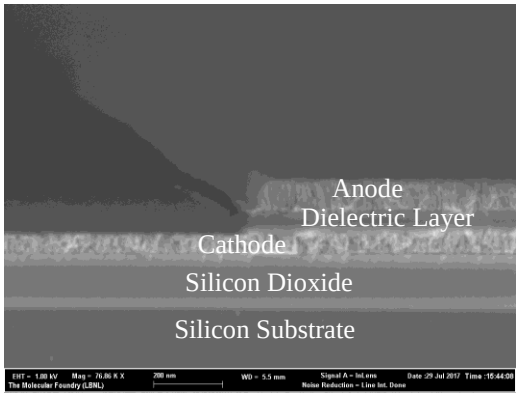

Figure 1. The SEM image of nanogap electrochemical cell.

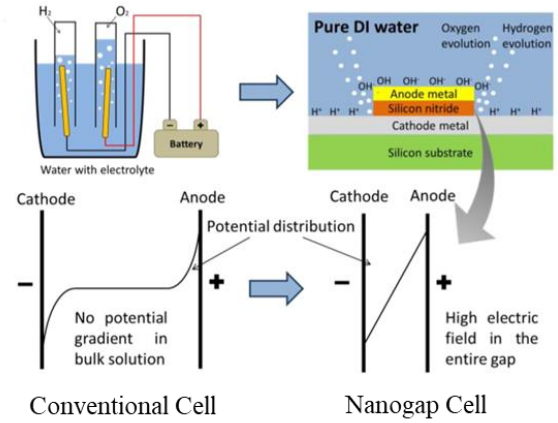

Figure 2. The schematic potential distribution in conventional and nanogap cell. [2]

Electro-oxidation at anode	$C_nH_{2n+1}OH + (2n\text{-}1)\ H_2O \rightarrow nCO_2 + 6nH^+ + 6ne^-$
Electro-oxidation at cathode	$6nH^+ + 6ne^- \rightarrow 3nH_2$
Overall Reaction	$C_nH_{2n+1}OH + (2n\text{-}1)\ H_2O \rightarrow nCO_2 + 3nH_2$

Table 1. The electro-oxidation at two electrodes and the overall electrochemical reaction. [3]

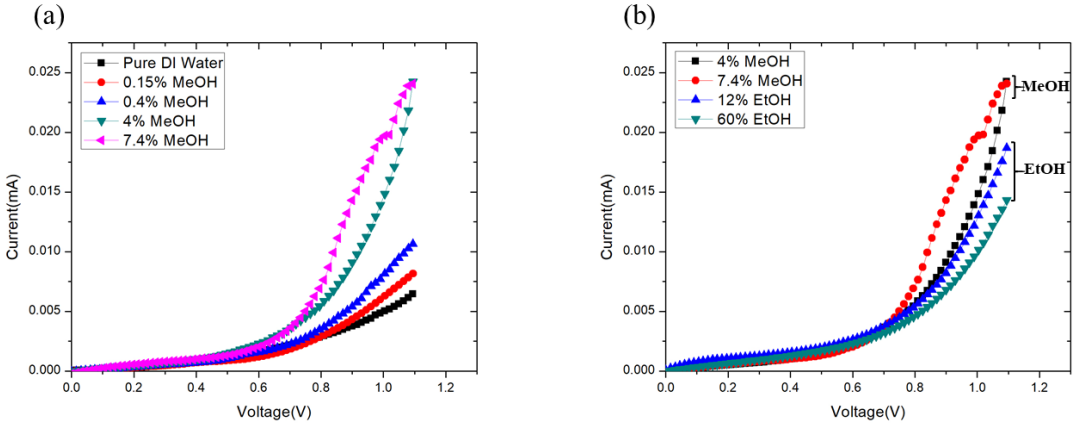

Figure 3 (a) The I-V curve of different volume concentrations of methanol in water solutions. (b) The I-V curve of different volume concentrations of methanol and ethanol in water solutions. Even in the high concentration ethanol solutions, the content of methanol can be detected indicating the enough sensitivity for the denatured alcohol detection.