Supplementary Material (ESI) for Energy & Environmental Science

Electronic Supplementary Information

On-chip fuel cells for safe and high-power operation: investigation of alcohol fuel solutions

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1. Electrodeposition of Pd-Co and Pt-Ru

All the electrodeposition procedures were carried out at room temperature (~25°C) in a conventional three-electrode cell. Pd-Co alloy was deposited by applying a constant current of –200 mA cm^{-2} for 60 sec (12 C cm^{-2}) in a solution containing 76 mM $[Pd(NH_3)_4]Cl_2$, 34 mM $CoCl_2$, 78 mM NH_4Cl, 120 mM Malonic acid, and NH_4OH (pH 9.1).[1] The loading was higher than that of our previous work, 5 C cm^{-2}.[2]

Pt-Ru alloy was deposited by applying pulse current (on: –50 mA cm^{-2}, 0.1 s; off: 0.5 s) to deposit 1 C cm^{-2} of Pt-Ru in a solution containing 20 mM H_2PtCl_6, 20 mM $RuCl_3$ and 0.002% $(CH_3COO)_2Pb$ on a Pt black layer predeposited by applying the same pulse current (1 C cm^{-2}) in a solution containing 20 mM H_2PtCl_6, 2 M HCl and 0.002% $(CH_3COO)_2Pb$.[1, 3]

2. Voltammograms for oxygen reduction reaction on Pd-Co catalyst in the presence of fuels

As a fundamental characteristics of Pd-Co catalyst, we have already reported that the oxygen reduction reaction (ORR) property of this alloy was hardly affected by the presence of methanol in acidic solution. Here, we reported that this alloy is also selective for the ORR in the presence of methanol, ethanol and 2-propanol both in acidic (Fig. S1) and neutral (Fig. S2) media.

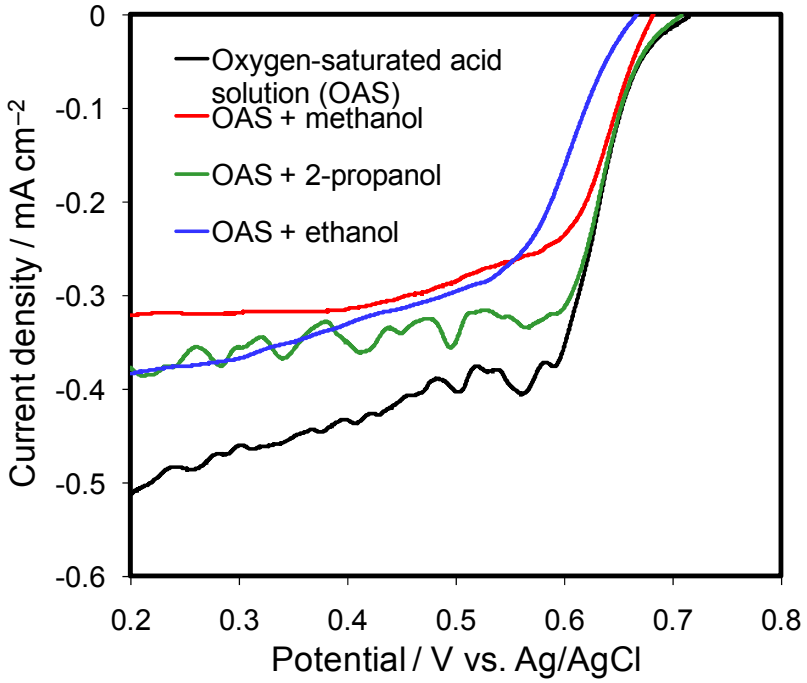

Fig. S1 Linear sweep voltammograms for oxygen reduction reaction on a Pd-Co alloy deposited by applying a constant current (1 C cm^{-2}). The data were obtained at room temperature in an oxygen-saturated 0.5 M H_2SO_4 solution containing 1 M fuel: methanol (red line), ethanol (blue line) or 2-propanol (green line). Scan rate: 1 mV s^{-1} (from open-circuit potential to 0.2 V vs. Ag/AgCl).

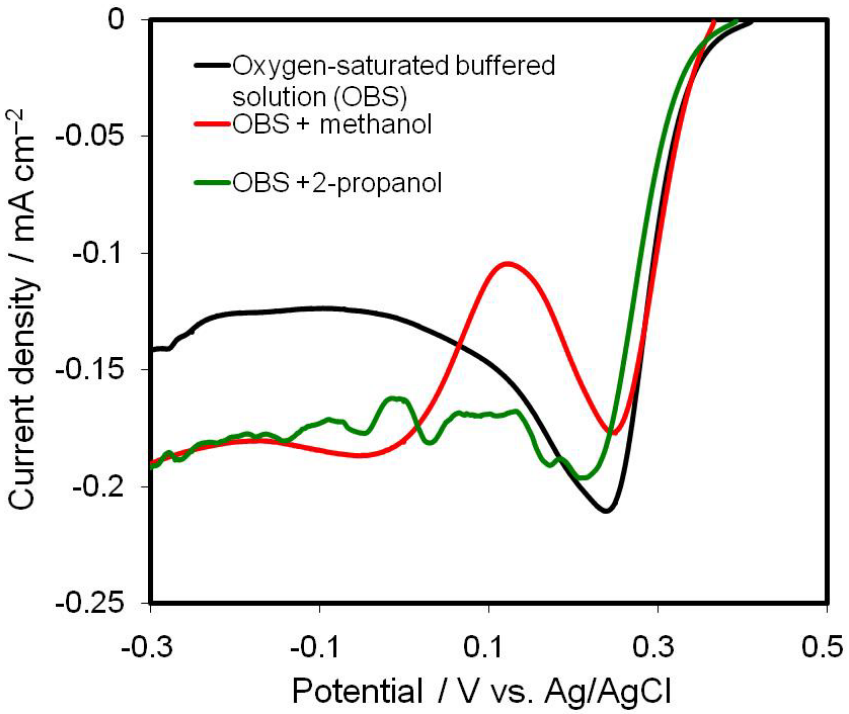

Fig. S2 Linear sweep voltammograms for oxygen reduction reaction on a Pd-Co alloy deposited by applying a constant current (1 C cm^{-2}). The data were obtained at room temperature in an oxygen-saturated phosphate buffer solution (0.25 M Na_2HPO_4 + 0.25 M KH_2PO_4) containing 1 M fuel: methanol (red line) or 2-propanol (green line). Scan rate: 1 mV s^{-1} (from open-circuit potential to 0.2 V vs. Ag/AgCl).

3. Endurance test (neutral methanol solution)

In the endurance test, a cell operating on an unbuffered methanol solution containing 0.5 M Na_2SO_4 as supporting electrolyte continued to generate power for 1 hour, but the performance was not stable (Fig. S1).[2] In contrast, a cell operating on a methanol solution containing phosphate buffer (0.25 M Na_2HPO_4 + 0.25 M KH_2PO_4) continued to generate electric power for at least 2 hours, and the performance was quite stable (Fig. S3).

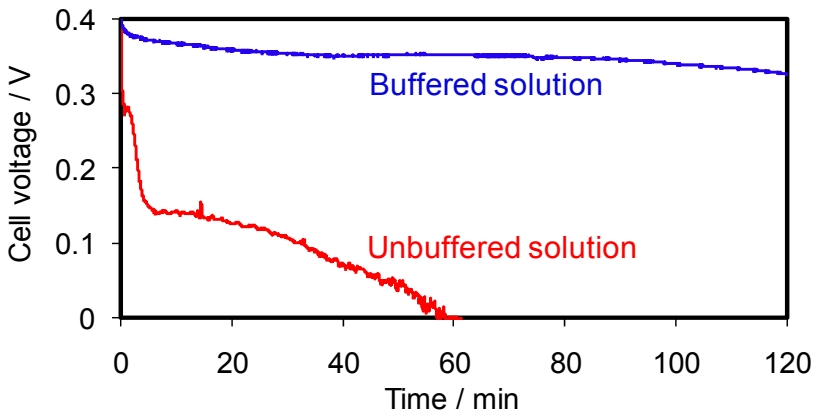

Fig. S3 Endurance test of the on-chip fuel cell operating on a methanol solution under the neutral pH condition (Blue line: buffered solution of 0.25 M Na_2HPO_4 + 0.25 M KH_2PO_4; Red line: unbuffered solution of 0.5 M Na_2SO_4). The cell voltages were recorded at 1.1 μA.

References

1. S. Tominaka, T. Momma and T. Osaka, *Electrochim. Acta*, 2008, **53**, 4679-4686.
2. S. Tominaka, S. Ohta, H. Obata, T. Momma and T. Osaka, *J. Am. Chem. Soc.*, 2008, **130**, 10456-10457.
3. T. Osaka, H. Iida, S. Tominaka and T. Hachisu, *Isr. J. Chem.*, 2008, **48**, 333-347.