

Supporting Information for

The Impact of the Alkali Cation on the Mechanism of the Electro-oxidation of Ethylene Glycol on Pt

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Experimental Section

Two working electrodes were used in this study: a platinum flag with geometric area of 0.27 cm^2 for conventional electrochemical experiments and a platinum disk of 0.80 cm^2 for the *in situ* FTIR experiments. All the potential are quoted versus a reversible hydrogen electrode (RHE) prepared with the same solution of the supporting electrolyte. To confection this electrode a high area platinised platinum flag was used to maintain the hydrogen exchanged current density high.¹ Solutions were prepared with high purity water (Milli-Q - $18.2\text{ M}\Omega\cdot\text{cm}$). Metal grade NaOH and KOH were provided from Sigma Aldrich and LiOH and ethylene glycol were provided by J. T. Baker. All chemicals were used as received. Aqueous solution consisting of 0.1 M ethylene glycol in 1.0 M LiOH, NaOH, or KOH were used as supporting electrolyte. The temperature was $20\text{ }^\circ\text{C}$. FTIR experiments were made in a Nexus 670 – Nicolet spectrometer with a MCT detector. The spectra have resolution of 8 cm^{-1} . Further experimental details are described elsewhere.^{2,3}

In situ IR results

Spectra were collected after the potential step from 0.05 V to 0.80 V. Single scans were collected in the region between 2300 to 1100 cm^{-1} and then the spectra was built by the co-addition at each of 2.5 s, resulting in about 13 scans per spectrum.

Figure S1 shows two sets of spectra for the electro-oxidation of 0.1 M ethylene glycol after 15 and 80 s following the potential step to 0.80 V. The base electrolyte was an aqueous solution 1 M of LiOH, NaOH, or KOH. Up to about 15 s two bands at 2030 and 1822 cm^{-1} are observed, and reflect the presence of linear and multi-bonded CO, respectively. An interesting feature of these bands is the shift to lower frequencies

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accompanying the increase in the cation radius. Additional features at 1410 and 1328 cm^{-1} indicate the presence of glycolate, whereas the band at 1587 cm^{-1} denotes the carbonyl symmetric stretching. This later does not help product identification since all of possible acid products show this band and it is merged with water band.

The CO and the glycolate bands disappear and new bands at 1404 and 1310 cm^{-1} indicate carbonate and oxalic acid as products, see spectra at 80 s in Figure S1. These bands increase in time. It is important to stress that at high pH and low EG concentration the electro-oxidation proceeds via production of carbonate and oxalate, other C2 products are found decreasing the pH or increasing EG concentration. Similar trend are found recently employing Pd as catalyst.⁴

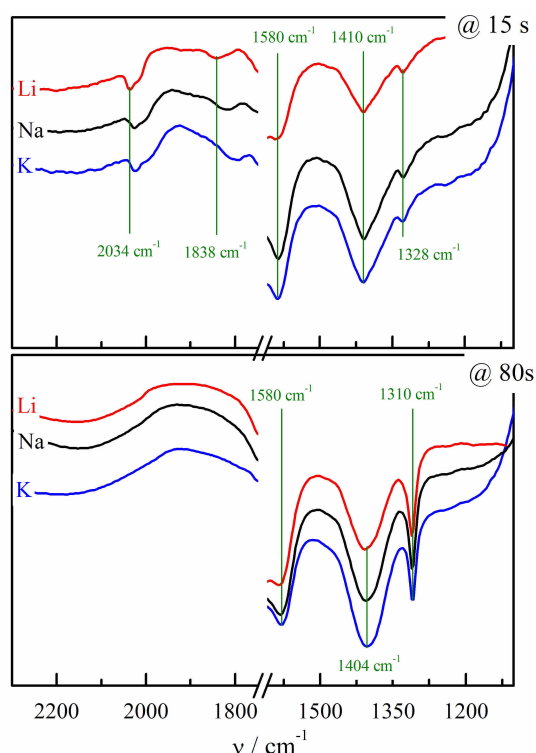


Figure S1: IR spectra obtained for the electro-oxidation of 0.1 M EG on platinum at 0.80 V and in the presence of 1.0 M MOH (M=Li, Na, or K).

References for Supporting Information

- 1 C. H. Hamman, A. Hammett and W. Vielstich. *Electrochemistry*, 2nd ed., Wiley, Weinheim, 2007.
- 2 E. Sitta, M. A. Nascimento and H. Varela, *Phys. Chem. Chem. Phys.*, 2010, **12**, 15195.
- 3 T. Iwasita and F.C. Nart, *Prog. Surf. Sc.* 1997, **55**, 271.
- 4 V. Bambagioni, M. Bevilacqua, C. Bianchini, J. Filippi, A. Marchionni, F. Vizza, L. Q. Wang and P. K. Chen, *Fuel Cells*, 2010, **10**, 548.