Supplimentary Information

The reaction path of methanol oxidation in alkaline medium on metal surface is expected to follow the same that occur on Pt or Pd electrode. The mechanism can be schematically represented⁵⁴ by:

- (i) $CH_3OH + M \longrightarrow M(CH_3OH)_{ad}$ (M = Ni)
- (ii) $M(CH_3OH)_{ad} + 4OH^- \longrightarrow M-CO + 4H_2O + 4e$
- (iii) $OH^- + M \longrightarrow M-OH + e$
- (iv) $M-CO + M-OH + OH^{-} \longrightarrow 2M + CO_2 + H_2O + e$
- (v) $CO_2 + 2OH^2 \longrightarrow CO_3^{2-} + H_2O$

Greater the analytical concentration of methanol, greater would be the formation of M-CO intermediate blocking the surface. At high positive potential, nickel and nickel hydroxide (M-OH) would be more tightly bound with the carboxylate anion of the polymer resulting non availability of M-OH around poisonous intermediate (M-CO) for surface cleansing reaction as indicated by eq. (iv). This is due to the formation of strong hydrogen bond between PAA and M-OH at high potential. The presence of the bulky organic moiety of the polymer near M-OH intermediate prevents surface diffusion of M-CO towards M-OH.⁵⁵

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