Luminescence Resulting from Electrocatalytic Oxidation of Simple Hydroxy Compounds at a Nickel Anode in Alkaline Media Containing a Fluorescent Dye

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(Received February 19, 1997; CL-970125)

Electrocatalytic oxidation of simple hydroxy compounds on a nickel(III) surface in alkaline media containing a fluorescent dye was demonstrated to lead to visible luminescence, probably due to energy transfer interactions between the fluorescent dye and oxidation products.

In alkaline media, the nickel electrode surface is covered with nickel(II) hydroxide ($Ni^{II}(OH)_2$),[1] and a nickel(III) oxide, generally presented as $Ni^{III}O(OH)$, is formed by the quasi reversible reaction (1):[2,3]

$$Ni^{II}(OH)_2 + OH^- \rightleftarrows Ni^{III}O(OH) + H_2O + e^- \quad (1)$$

As reported previously, the nickel(III) surface is active toward oxidation of simple hydroxy compounds in alkaline media.[2,4,5] In this study, we showed that the oxidation of these hydroxy compounds at the nickel anode in the presence of an adequate fluorescent dye generates luminescence in visible spectrum. We report here typical luminescent reactions with ethanol and glucitol in NaOH solutions containing 8-hydroxypyrene-1,3,6-trisulfonic acid (HPTS) as a fluorescent dye.

A nickel working electrode (1.5 mm in diameter; BAS Inc.) was polished to a mirror-like finish with a 0.5-μm alumina suspension. The electrode potential was monitored with respect to a Ag/AgCl reference electrode, 3 M (= mol dm^{-3}) NaCl (BAS). A measurement system with an opto-electrochemical cell followed the previous report.[6] Anodically initiated luminescence spectra were taken with a Shimadzu spectrofluorophotometer (Model RF 540) with an excitation lamp-off. To measure spectra, luminescence was repeatedly stimulated by means of symmetry square wave electrolysis between - 0.20 and + 0.45 V, with a pulse width of 1.0 s, during wavelength scanning. To complete one spectral recording, ca. 100 cycles of the square wave potential pulse were applied. The luminescence intensity was kept constant under the pulsed conditions above. Measurements were performed at 22 ± 2 °C.

Figure 1 shows typical cyclic voltammograms and corresponding light emission profiles. For the 1.0 M NaOH solution free from ethanol and glucitol, a pair of anodic and cathodic waves centering at about + 0.3 V would be due to the formation of $Ni^{III}O(OH)$ and regeneration of $Ni^{II}(OH)_2$.[2,7] There were no differences in cyclic voltammograms in the presence and absence of 20 μM HPTS. Noticeably, the addition of ethanol or glucitol enhanced the oxidative current responsible for the formation of $Ni^{III}O(OH)$ at about + 0.4 V, followed by the appearance of a luminescence peak. The abrupt current rise observed at more positive potentials was due to the oxidation of hydroxide ions. The luminescence intensity seemed irrelevant to the number of hydroxy groups of the substrate molecule unlike the oxidative current around + 0.4 V which increased with increase in number of hydroxy groups. In the absence of HPTS, the oxidation of hydroxy compounds at the nickel anode did not give rise to visible radiation. This result was distinct from that observed at the glassy carbon anode where weak visible luminescence was generated even in the absence of a fluorescent dye.[8] Background emission due to the electro-oxidation of HPTS was negligible on the nickel anode.

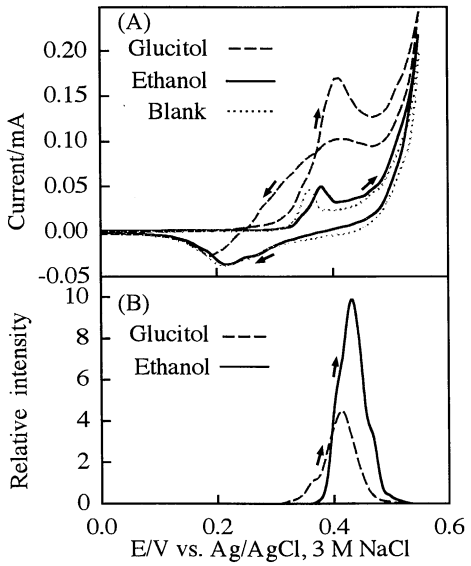

Figure 1. Cyclic voltammograms of solutions composed of 1.0 M NaOH and 20 μM HPTS with and without hydroxy compounds (A) and correponding luminescence curves (B); both were depicted ranging from 0.0 to + 0.6 V. Potential scan started positively from - 0.1 V at 20 mV/s. [Ethanol] and [Glucitol], 10 mM each. Luminescence of the blank solution (1.0 M NaOH containing 20 μM HPTS) was negligible.

Table 1. Peak potentials for oxidative and luminescent waves (E_{ox} and E_{em}, respectively), peak oxidative current (i_p) and peak luminescence intensity (L_p) as a function of [NaOH]

Alkalinity	Ethanol				Glucitol			
(NaOH, M)[a]	E_{ox}[b]	E_{em}[b]	i_p(μA)	L_p[c]	E_{ox}[b]	E_{em}[b]	i_p(μA)	L_p[c]
0.04	0.49	0.55	66	0.01	0.58	0.54	127	0.01
0.1	0.47	0.54	86	0.04	0.52	0.51	172	0.08
0.4	0.42	0.50	109	0.42	0.48	0.48	238	0.60
1.0	0.39	0.48	116	1	0.44	0.46	237	1
4.0	0.34	0.47	128	1.93	0.40	0.40	217	0.26

[a] Each solution contained 20 μM HPTS and ethanol or glucitol (10 mM each). [b] E vs. Ag/AgCl, 3 M NaCl. [c] Normalized to the L_p value at 1.0 M NaOH in each column. Results were obtained in linear potential sweep experiments at 100 mV/s.

As presented in Table 1, the increase in NaOH concentration caused a rise in the oxidative current and a shift in its peak potential in the cathodic direction, except in the case of glucitol at higher NaOH concentrations. This is probably because the formation of the active nickel(III) surface is facilitated by

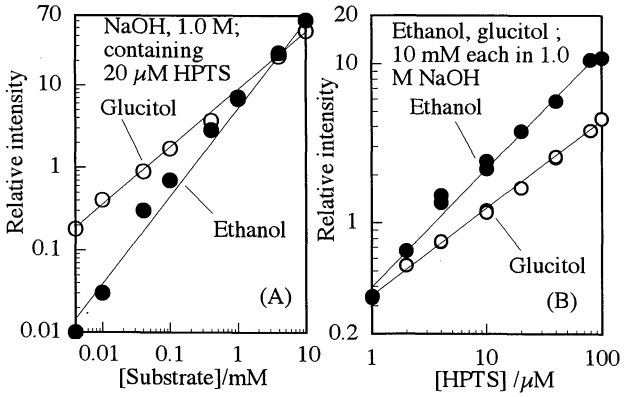

Figure 2. Plots of relative intensity vs. concentrations of substrates (ethanol and glucitol) (A) and HPTS (B). Relative intensity, peak luminescence intensity, measured by linear potential scan at 100 mV/s (A) and 20 mV/s (B).

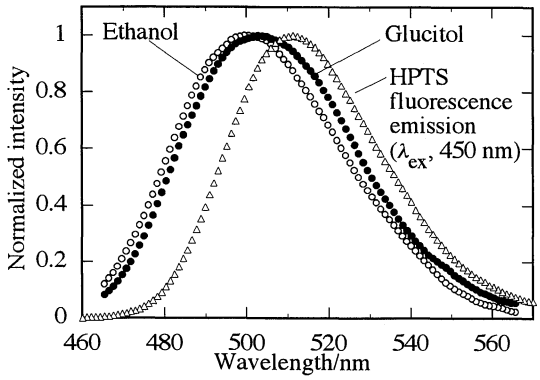

Figure 3. Luminescence spectra resulting from the oxidation of ethanol and glucitol at the Ni anode in 1.0 M NaOH containing 80 μM of HPTS and fluorescence emission spectrum of 80 μM HPTS in 1.0 M NaOH containing ethanol or glucitol. [Ethanol] and [Glucitol], 10 mM each.

increasing solution alkalinity, based on the report that the oxidation of $Ni^{II}(OH)_2$ to $Ni^{III}O(OH)$ is of the first order with respect to hydroxide ion.[5] Importantly, the changes in the luminescence intensity and its peak potential as a function of NaOH concentration substantially conformed to those in the oxidative current and its peak potential. At a fixed NaOH concentration, the peak luminescence intensity varied directly with concentrations of substrate and HPTS over a wide concentration range (Figures 2 A and B).

The results obtained by the linear potential sweep experiments indicate that the luminescence is triggered by the electrocatalytic oxidation of ethanol and glucitol on the nickel(III) surface in the presence of HPTS and that the interaction between HPTS and oxidation products is important for emission of light. In terms of potentials required for light emission, the nickel anode is much more advantageous than the glassy carbon anode where the luminescent oxidation of hydroxy compounds occurred around + 1.4 V.[8] Stronger alkalinity, which usually causes degradation of carbohydrates, may be responsible for the drop of luminescence intensity concomitant with the oxidative current drop in the case of glucitol at NaOH concentrations over 1 M.

Luminescence spectra from the oxidation of ethanol and of glucitol at the nickel anode in 1.0 M NaOH solution containing 80 μM HPTS were nearly identical (Figure 3). Note that the luminescence spectra shifted by about 10 nm in the shorter wavelengths and were somewhat broader as compared to the fluorescence emission spectrum of 80 μM HPTS in 1.0 M NaOH containing 10 mM ethanol or glucitol, which was probably from the excited HPTS monomer (HPTS*). The fluorescence emission spectrum of a sample solution with excitation at 450 nm after the pulsed electrolysis for measurement of the luminescent spectrum was essentially the same as that before.

Based on the spectral results and the important observation that the oxidation of hydroxy compounds on the nickel(III) surface in the absence of HPTS did not lead to perceptible visible luminescence, it is suggested that the mechanism of energy transfer between oxidation products (D* species) and HPTS as an energy acceptor forms light emissive intermediates, resulting in visible luminescence with a maximum at about 500 nm and that HPTS is not consumed in this luminescent reaction. From the linear relationship between luminescence intensity and concentrations of substrate and HPTS (Figures 2 A and B), it is suggested that formation of the light emissive intermediate is the result of bimolecular energy transfer interaction between D* species and HPTS. The most likely light emissive intermediate is D---HPTS* converted by energy transfer from an initially formed encounter complex (D*---HPTS).

A fairly good agreement between the luminescence spectra for ethanol and for glucitol suggests that D* species in both cases resemble one another, and those could be excited carbonyl products, resulting from their oxidation.[8] From the observation that no change was observed in cyclic voltammograms of ethanol and glucitol in the presence and absence of HPTS, the ground state interaction between these hydroxy compounds and HPTS would be neglected in this luminescent reaction.

It is not clear why visible radiation is not observed in the oxidation of hydroxy compounds on the nickel(III) surface in the absence of HPTS unlike the case of the glassy carbon surface.[8] Further characterization of D* species and the energy transfer interaction described above is under way.

This work was supported by Grant-in-Aid for Scientific Research (C) No. 07804047 from the Ministry of Education, Science and Culture, Japan.

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