Electrochemical Hydrogenation Mechanism of ANDMU on Platinum and Nickel electrode

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The hydrogenation of 6-amino-5-nitroso-1,3-dimethyluracil(ANDMU) as an intermediate of commercially synthesized caffeine is generally carried out using iron powder reduction or Raney nickel catalyst. However the iron powder results in serious pollution and the Raney nickel catalyst needs an expensive hydrogen supply system operated under severe conditions. A green chemical technology using an electrochemical hydrogenation process can eliminate the pollution and the unsafe conditions.

The Electrochemical hydrogenation mechanism of ANDMU on Platinum and Nickel electrode was studied by steady state polarization curves, cyclic voltammetry and constant-potential coulometry in pH 3 aqueous solution. By cyclic voltammetry one irreversible peak was found in the range of -600~-800 mV (vs Hg_2SO_4) on Platinum electrode. The potential range is just the hydrogen adsorption range. The numbers of electrons and hydrogen ions involved in the electrochemical reaction are both 4. While the numbers of them are both 1 involved in the rate-determined step. Based on these facts, the mechanism could be concluded that hydrogen ions are reduced on the electrode surface to adsorbed atomic hydrogen then the adsorbed atomic hydrogen reduce ANDMU near and adsorbed on the electrode. The reaction is controlled by diffusion and the reaction rate increased with increasing temperature and stirring speed and with decreasing pH. The data in the experiments of ANDMU hydrogenation on Nickel electrode lead to the same conclusion as that on Platinum electrode. It was deduced that and the hydrogenation of ANDMU either on Platinum or on Nickel electrode is an electrocatalytic process.
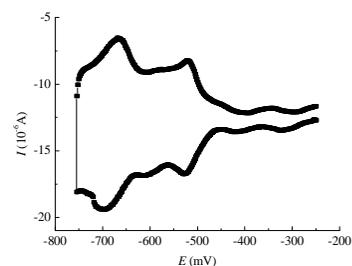

Fig. 1 Hhydrogen adsorption on Pt electrode in solution without ANDMU
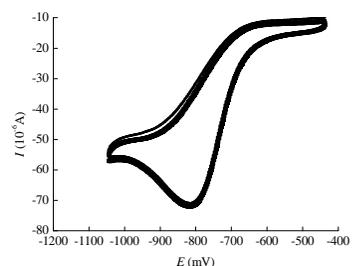

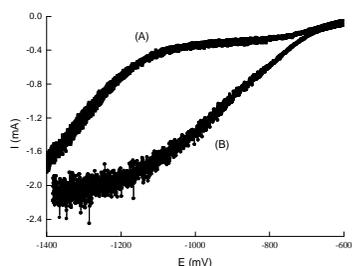Fig. 2 ANDMU hydrogenation on Pt electrode in solution with ANDMU

Fig. 3 Steady state polarization curves on Ni electrode A-without ANMDU;B-with ANDMU
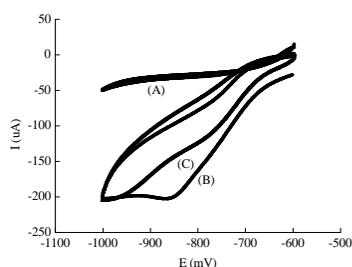

Fig. 4 Cyclic voltammogram of ANDMU on Ni electrode A-without ANDMU;B-first cycle with ANDMU;C-latter cycle with ANDMU
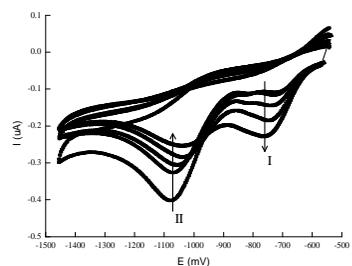

Fig. 5 change ANDMU concentration

Potention (mV)	ANDMU (mg)	Q (C)	n
-850	2.64	5.21	3.8
-850	2.03	4.61	4.3
-850	1.59	3.50	4.2

Table 1 Determination of electrons number by constant-potential coulometry on Pt electrode

Potention (mV)	ANDMU (mg)	Q (C)	n
-900	4.75	9.80	3.93
-900	5.50	11.12	3.88
-900	2.38	4.62	3.70

Table 2 Determination of electrons number by constant-potential coulometry on Ni electrode