

Support information

1. Chemical dynamic analysis

The chemical dynamic equation can be written as:

$$- \frac{d c(\text{Cr(III)})}{dt} = k * c(\text{Cr(III)}) * c(\text{OH}^-)$$

In this equation, k is the chemical reaction constant, and $c(\text{Cr(III)})$ is the concentration of Cr(III) . Because the concentration of OH^- in solution is a lot, and the relative consumption in the reaction process is less. So we can ignore the effect of OH^- , and the reaction is viewed as pseudo first order kinetics.

The kinetic equation of the reaction can finally be written as:

$$\ln c(\text{Cr(III)}) = -kt$$

The Kinetic fitting results of the oxidation reaction of Cr(III) in different pH can be seen in Fig.6.

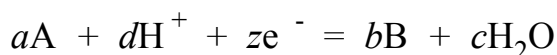
In addition, we can establish the relationship between the chemical reaction constant and the temperature by Arrhenius equation, which can be written as:

$$\ln k = \frac{-E_a}{RT} + \ln A$$

E_a is the activation energy, while A is frequency factor. Kinetic fitting results of the oxidation reaction of Cr(III) in different temperature and the relationship of $\ln k - 1/T$ can be seen in Fig.7.

2. Thermodynamic calculation

In the discussion of the electrochemical system composed of metallic oxide and water, we can illustrate a half cell reaction as follows:



Where a, d, b, c represent the number of reaction cells of species A, H^+ , B, H_2O . The z is the number of electrons translated in this reaction. In dilute solution, $a(H_2O)$ is similar to 1 for the activity of water. The relationship between electrochemical electromotive force and activity of various substances involved in battery reaction can be expressed as Nernst equation:

$$E_T = E_T^\ominus - \left[\frac{RT}{zF} \right] \lg \frac{a_B^b}{a_A^a a_{H^+}^d}$$

$$\text{Besides, } \text{pH} = -\lg a(H^+), \lg k = \ln k / 2.303$$

$$\text{So, } E_T = E_T^\ominus - [2.303RT/zF] \lg \frac{a_B^b}{a_A^a} - [2.303dR/zF] \text{pH}$$

In the equation, E_T and E_T^\ominus are in behalf of electrochemical potential or standard electrochemical potential at appointed temperature. $a_B^b, a_A^a, a_{H^+}^d$ are certain times overall activity of each species. F and R is corresponding to Faraday's constant and molar gas constant. At last, we can get the relationship between G and E by equilibrium constant K:

$$\Delta_r G_T^\ominus = -zFE_T^\ominus = -RT \ln K^\ominus$$

$\Delta_r G_T^\ominus$ is Gibbs free energy of standard electrochemical reaction, and K^\ominus is standard equilibrium constant of the reaction. In general, we can get the ΔG -pH diagram at the certain temperature and ionic activity with the

relationship of pH, E_T and $\Delta_r G_T^\ominus$.