

Supporting information

For the evaluation of the electrolyte diffusion coefficient, the Rotating Disk Electrode (RDE) methodology was selected. An IVIUM potentiostat was used together with a motor controller in the range from 2000 to 4000 rpm. The working electrode selected was a glassy carbon disk with a diameter of 5 mm embedded in a PTFE rod. Ag/AgCl and a Pt electrodes were selected as reference and counter electrode respectively. From now on all the potentials are referred to the Ag/AgCl (KCl sat.) reference electrode. The methodology is based on the Levich approximation [1], where the limiting current at the RDE is expressed as a function of the diffusion coefficient:

$$i_l = 0.6208 n F D^{2/3} \Omega^{1/2} \nu^{-1/6} C_0 \quad (S1)$$

where n is the number of electrons involved in the reaction, F the Faraday constant, D the diffusion coefficient of the considered species, Ω the rotation speed, ν kinematic viscosity and C_0 the concentration of the species. A linear sweep voltammetry was carried out from 0 to 1.5 V at room temperature and from -0.5 to +0.5 V at 120°C due to the shift at lower potential of the reduction peak. A scan rate of 50 mV/sec was used and the limiting current was registered from 2000 to 4000 rpm with an interval of 500 rpm. For the diffusion coefficient evaluation, the limiting current in Ampere is plotted against the square root of the rotation speed in Rad/s, from the trend line the slope is extrapolated and used in the following formula derived from Equation (S1):

$$D^{2/3} = \frac{m}{0.6208 n F A C_0 \nu^{-1/6}} \quad (S2)$$

Where m is the slope and A is the area of the electrode.

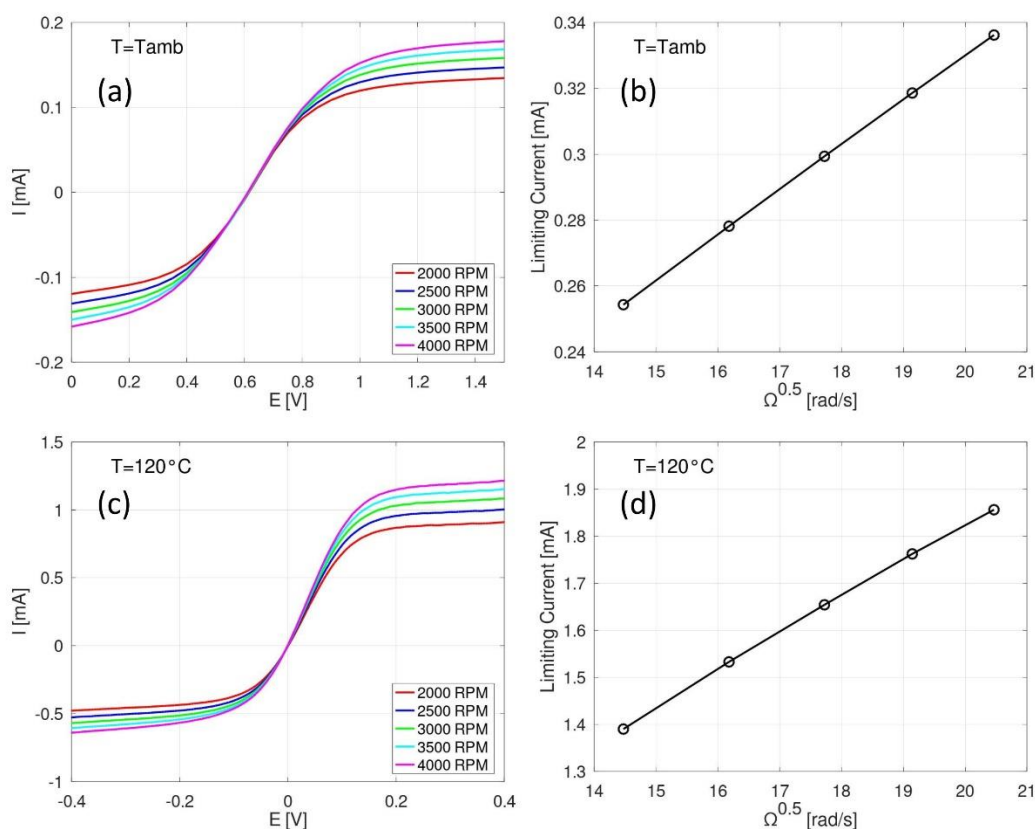


Figure S1. Voltammetries with rotating disk electrode at ambient temperature and 120°C (left). Relationship between current and square root of the angular velocity of the RDE (right).

The diffusion coefficient at room temperature is $1.7 \cdot 10^{-7} \text{ cm}^2/\text{s}$, while at 120°C $2.7 \cdot 10^{-6} \text{ cm}^2/\text{s}$. Once the diffusion coefficient is calculated is possible to use it in the Randles-Sevcik law [1] for the evaluation of the electrochemical surface area (ECSA):

$$i_p = 2.686 \cdot 10^5 n^{3/2} A D^{1/2} C \nu^{1/2} \text{ (S3)}$$

Where A is the electrochemical surface area in cm^2 , i_p is the peak current in Ampere, n is the number of electrons involved in the reaction, D is the diffusion coefficient in cm^2/s , C is the molar concentration of the electroactive species in mol/cm^3 and ν is the scan rate in V/s .

A small disk of 2 cm of diameter was obtained from the four samples analyzed and immersed in the ionic liquid-based electrolyte containing the $[\text{Co}(\text{ppy})]^{3+/2+}$ redox couple. Two Pt electrodes were selected as pseudo-reference and counter electrode, since Ag/AgCl is not suitable for temperatures over 100°C . The cyclic voltammetries were acquired in a steady-state condition under N_2 flux to maintain an inert atmosphere without oxygen or humidity. Different scan rates were implied starting from 5 to 30 mV/s every 5 mV/s , then the peak current in Ampere is plotted against the square root of the scan rate. The slope is necessary to calculate the electrochemical surface area based on the following equation derived from Equation (S3):

$$A = \frac{m}{2.686 \cdot 10^5 n^{3/2} D^{1/2} C} \text{ (S4)}$$

References

1. Bard, A.J.; Faulkner, L.R. *Electrochemical Methods : Fundamentals and Applications*; New York : Wiley, 2001; ISBN 978-0-471-04372-0.