

The Significant Effect of Supporting Electrolytes on the Galvanic Deposition of Metallic Rhenium

Huazhen Cao, Lilong Hu, Huibin Zhang, Guangya Hou, Yiping Tang, Guoqu Zheng*

College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou, 310014, China

*E-mail: zhenggq@zjut.edu.cn

Received: 1 March 2020 / *Accepted:* 29 April 2020 / *Published:* 10 June 2020

The effects of a supporting electrolyte (Na_2SO_4) on the galvanic deposition of metallic rhenium from acidic ammonium perrhenate aqueous solution were investigated. The results show that the supporting electrolyte plays an important role in the galvanic deposition of metallic rhenium. The main product in the more concentrated NH_4ReO_4 solution is only rhenium oxides in the absence of supporting electrolyte due to substantial hydrogen evolution reaction (HER). However, the introduction of a supporting electrolyte enhances the activation energy of the HER, resulting in the formation of metallic rhenium. The current efficiency is as high as 31.4% under optimized conditions, which is far above the values previously reported.

Keywords: metallic rhenium; electrodeposition; supporting electrolyte; sodium sulfate

1. INTRODUCTION

Since the 1950s, the unique properties of rhenium have inspired a number of studies on the properties of rhenium and its alloys[1-4]. In these studies, the preparation of metal rhenium is the most basic and important issue. The high cost of rhenium precludes its extensive use in large structural components. In addition to its scarcity, the complexity of the manufacturing process of metal rhenium is another issue contributing to its high price. Most of the published reports to-date deal with the fabrication of rhenium powder by thermal reduction of pure ammonium perrhenate in hydrogen[5-7], which is an expensive, complex and energy intensive process.

Electroplating at near-room temperature using a nontoxic bath may be a reasonable alternative[8-10]. However, rhenium belongs to a group of metals that are difficult to produce by electrolysis from aqueous solutions, mainly because of its very low overpotential for the hydrogen evolution reaction[11-13]. The E_h -pH diagram of Re- H_2O indicates that both the potential and pH must be finely controlled to maximize the deposition of metallic Re and minimize the hydrogen evolution.

Our prior studies revealed the multi-step electroreduction mechanism of ReO_4^- to Re[14], and pointed out the positive role of high acidity and low ReO_4^- concentration in electrodepositing metallic rhenium. However, a high ReO_4^- concentration usually leads to the formation of rhenium oxides[15-16], which reduces the overpotential for the HER and decreases the current efficiency. Therefore, although the reduction of ReO_4^- to Re is thermodynamically feasible, the cathodic current efficiency is very low. For example, previous studies by Netherton and Holt found that the sulfuric bath was the most satisfactory rhenium plating bath[17], but the current efficiency was no more than 15%. In recent decades, very little research has been done to improve the electrodeposition of metallic rhenium. Schrebler and co-workers studied the nucleation and growth mechanisms for rhenium, and the Faradic yield for this process was 12–20%[18]. To date, no studies have reported an effective way to enhance the current efficiency of rhenium electrowinning from aqueous solutions. This paper introduced the positive role of sodium sulfate as a supporting electrolyte for rhenium deposition, by which the current efficiency was increased considerably. Additionally, the main mechanism was detailed via electrochemical investigation.

2. EXPERIMENTAL

The galvanic deposition was conducted in an open system using copper as the cathode and platinum as the anode. All the electrolytes were freshly prepared with analytic grade NH_4ReO_4 , H_2SO_4 and Na_2SO_4 . All the components were dissolved in double-distilled water. The experiments were performed at 70 °C for 2 h under magnetic stirring.

For the quantitative analysis of the metallic rhenium product under different concentrations of supporting electrolyte, galvanostatic discharge curves were measured on a CHI660 electrochemical workstation using a glassy carbon electrode (GCE, 12.566 mm²) as the working electrode, platinum plate as the counter electrode and platinum wire as the reference electrode. First, a short time (i.e. 10 min) deposition process was conducted at a current of -2 mA, after which the discharge process was performed with a discharge current of 1 mA. For the cyclic voltammetry curve (CV) and polarization curve measurements, a saturated calomel electrode (SCE) was selected as the reference electrode. The scan rates for the CV and polarization curve measurements were 10 mV s⁻¹ and 1 mV s⁻¹, respectively.

The surface morphology and composition of the products were characterized by atomic force microscopy (AFM, Edge Dimension), X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha+) and X-ray diffraction (XRD, Panalytical X'Pert PRO). Considering the amorphous structure of the electrodeposited rhenium, before XRD measurements, thermal treatment was conducted on all the samples in an argon atmosphere at 500 °C for 3 hours.

3. RESULTS AND DISCUSSION

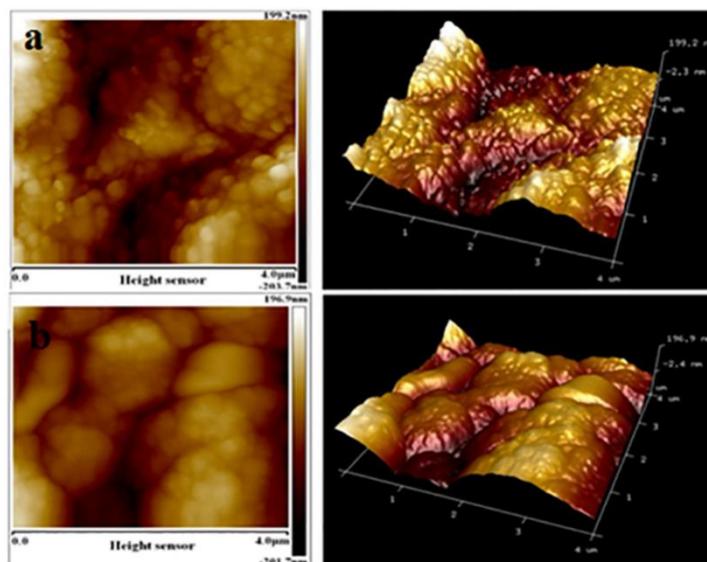
3.1 Morphology and composition analysis

Fig. 1a and 1b shows three-dimensional AFM images of the rhenium products, from which we can clearly see the difference between the two samples prepared in solutions with and without the

supporting electrolyte. In the case of lacking Na_2SO_4 , the average particle size of the product is relatively small, and the roughness is approximately $0.0522 \mu\text{m}$. In the presence of Na_2SO_4 , the average particle size of the product becomes larger and its surface roughness decreases to $0.0416 \mu\text{m}$. This result indicates that the addition of Na_2SO_4 is advantageous to the surface flatness of the rhenium product.

The phase composition of the products was analysed by XRD. As Fig. 1c and 1d shows, the product in the presence of the supporting electrolyte is quite different from that without supporting the electrolyte. The diffraction peaks of metallic rhenium are very weak in the absence of Na_2SO_4 , while the diffraction peaks of rhenium oxides (i.e., ReO_2 and ReO_3) are strong in this case. When Na_2SO_4 is introduced to the electrolyte, the main product changes to metallic rhenium and no other impurity peaks are observed. That is, the addition of Na_2SO_4 benefits the deposition of metallic rhenium.

Fig. 1e and 1f shows the XPS narrow-spectrum of the $\text{Re}4f$ of the deposited products. The peak separation is performed by XPS PEAK41 software. The Gaussian/Lorentzian ratio (G/L) is fixed at 30%. The difference in the orbital energy of $\text{Re} 4f_{7/2}$ and $\text{Re} 4f_{5/2}$ is approximately 2.43 eV [19]. The results show that in the absence of Na_2SO_4 , the deposition product is a mixture composed of metallic rhenium (41.0 eV) and a large number of rhenium oxides, i.e., ReO_2 (43.1 eV) and ReO_3 (45.0 eV)[20]. After the addition of $2 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ to the electrolyte, the product yields a strong doublet with a $\text{Re} 4f_{7/2}$ peak at 40.7 eV , this doublet corresponds to metallic rhenium. In addition, a weak peak of Re/O_2 appears at 41.7 eV , and its binding energy is higher than that of Re (40.7 eV), but lower than that of ReO_2 (43.1 eV), which is caused by the adsorption of oxygen on the surface of the metallic rhenium, rather than the peak of rhenium oxide[19,21].



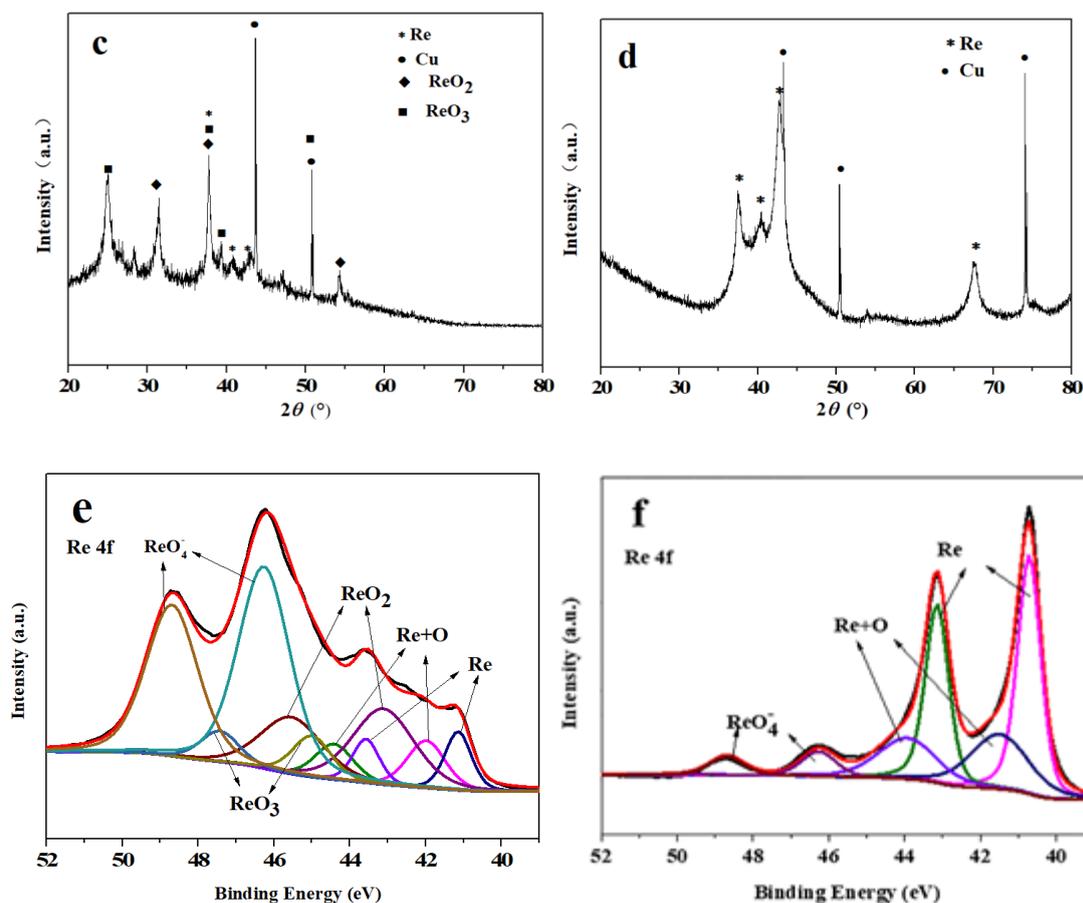


Figure 1. 3D AFM images(a, b) and XRD(c, d), XPS(e, f) patterns of deposited products prepared from solutions containing $0.075 \text{ mol L}^{-1} \text{ NH}_4\text{ReO}_4$, $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and different Na_2SO_4 concentrations, (a), (c), (e) without Na_2SO_4 , and (b), (d), (f) with $2 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$.

3.2 Current efficiency for rhenium electrodeposition

Fig. 2 displays the dependence of the current efficiency on the supporting electrolyte under different NH_4ReO_4 concentrations. It can be seen that in the absence of Na_2SO_4 , the current efficiency is extremely low, no more than 14%. Moreover, unlike conventional metal deposition, herein, increasing the NH_4ReO_4 concentration leads to a decrease in the current efficiency. Our previous studies stated that the electroreduction of ReO_4^- to Re is a multi-step process involving the successive reduction of intermediate and high ReO_4^- concentration triggers the production of a detrimental intermediate (i.e. ReO_2), that is a catalyst for HER. Therefore, some studies considered a low ReO_4^- concentration to be advantageous to the electrodeposition of metallic rhenium[14].

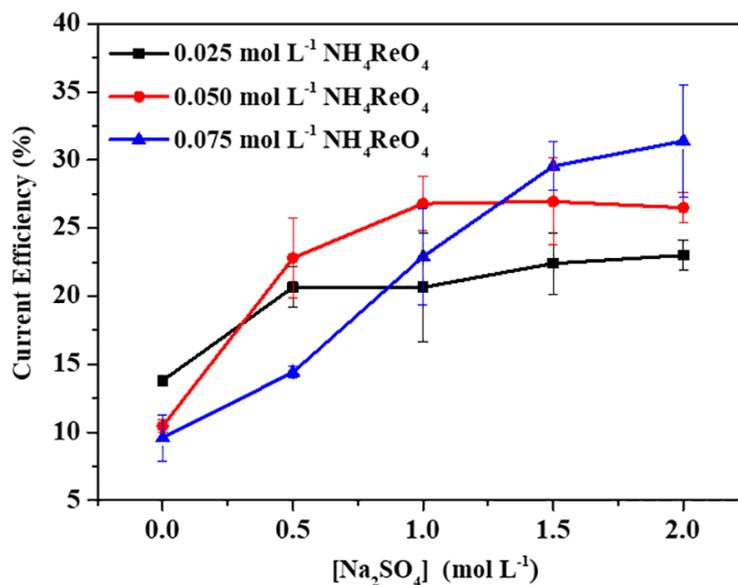


Figure 2. The dependence of the current efficiency on the sodium sulfate concentration under different concentrations of ammonium perrhenate ($0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, $t=7200 \text{ s}$, $T=70 \text{ }^\circ\text{C}$).

However, in this study, we find that the introduction of the supporting electrolyte produces unexpected results. It accelerates the mass transfer of ReO_4^- , depresses the production of ReO_2 and effectively reduces the HER side-reaction. As Fig. 3 shows, in the case of low Na_2SO_4 concentration or without Na_2SO_4 , a significant decrease in current efficiency is observed with increasing ReO_4^- concentration. However, when the Na_2SO_4 content is high enough (i.e., $\geq 1.5 \text{ mol L}^{-1}$), the current efficiency increases considerably with increasing the NH_4ReO_4 concentration, and the maximum value reaches 31.4%, which is much higher than the reported values ($\leq 20\%$)[18]. We also investigated the case of higher Na_2SO_4 concentrations, but the current efficiency no longer increases.

3.3 Galvanostatic discharge study

For the ammonium perrhenate aqueous solution, rhenium oxides are easily generated during the electrodeposition process, accompanied with serious hydrogen evolution. For example, the studies by Szabó and Bakos have revealed the formation of ReO_2 in a diluted sulfuric acid solution and Re_2O_5 in a concentrated solution[22]. Schrebler et al obtained a mixed oxides of ReO_3 , ReO_2 and Re_2O_3 in the potential below HER and metallic rhenium can only be prepared in the potential region of HER[23]. Vargas-Uscategui et al investigated the alkaline electrolyte and found the coexistence of metallic rhenium and rhenium oxide on cathode[24]. In order to acquire the exact information about the amount of metallic rhenium products under different supporting electrolyte concentrations, a series of galvanostatic discharge curves for different electrodeposited samples were measured and the corresponding results are shown in Fig. 3a-c. As seen from the figures, all the samples exhibit a discharge plateau (AB) at approximately -0.25 V (vs Pt), that corresponds to the oxidation of metallic Re. After the plateau, there is a short transitional region (BC) with a small slope in the curves, which may be ascribed to the further oxidation of low-valence rhenium oxides. From the duration of the

plateau, a more accurate evaluation of the role of the supporting electrolyte can be obtained (Fig. 3d). As the supporting electrolyte concentration increases, more metal rhenium is deposited, leading to a longer platform. Furthermore, the effects of the supporting electrolyte present a similar tendency, as shown in Fig. 2. Under a high concentration of supporting electrolyte, metallic rhenium can be fabricated from a more concentrated ammonium perrhenate aqueous solution with improved current efficiency, further supporting its positive role in the electroreduction of metallic rhenium.

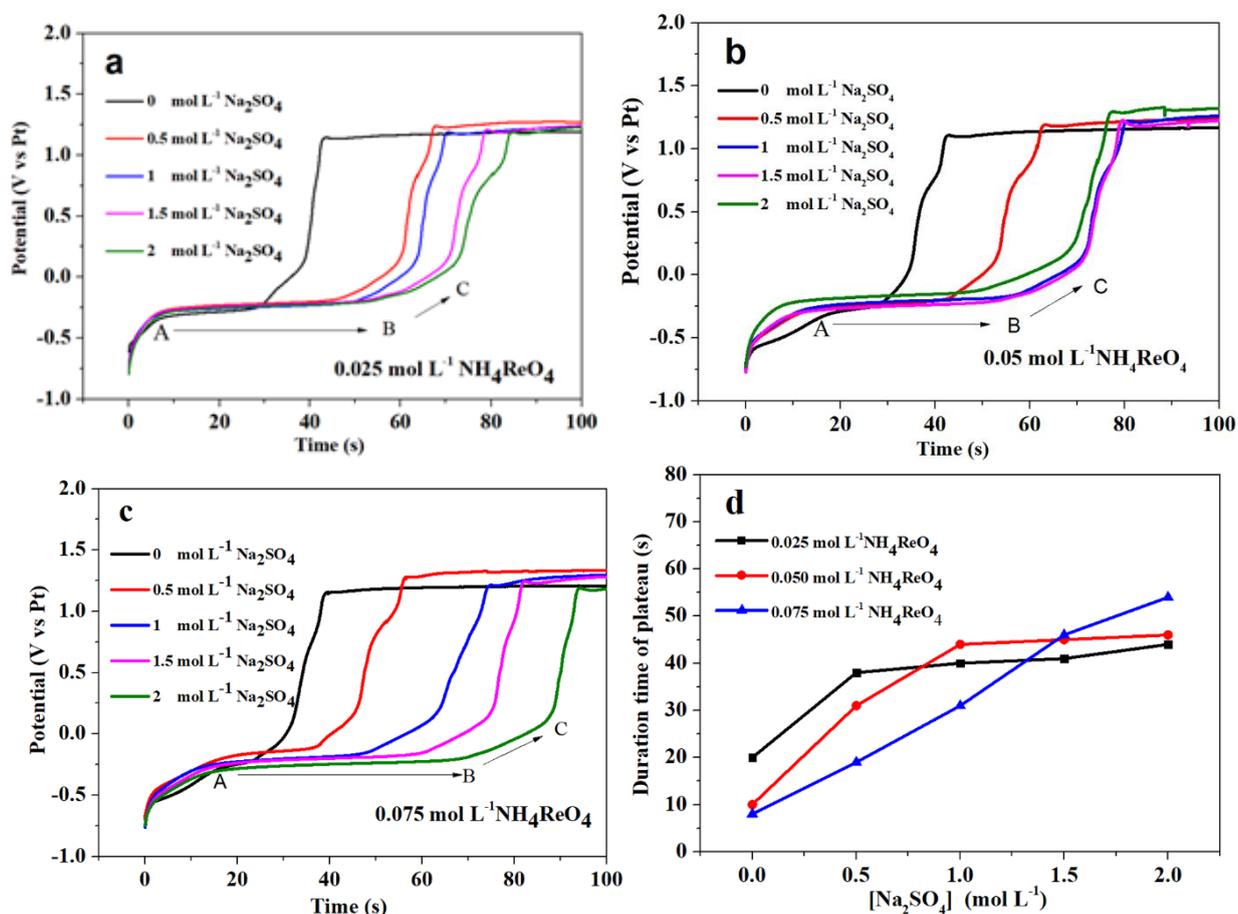


Figure 3. Discharge curves of the samples electrodeposited from different solutions at $70 \text{ }^\circ\text{C}$: a) $0.025 \text{ mol L}^{-1} \text{ NH}_4\text{ReO}_4$, $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and different Na_2SO_4 concentrations; b) $0.05 \text{ mol L}^{-1} \text{ NH}_4\text{ReO}_4$, $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and different Na_2SO_4 concentrations; c) $0.075 \text{ mol L}^{-1} \text{ NH}_4\text{ReO}_4$, $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and different Na_2SO_4 concentrations; d) the relationship between the duration of the plateau and the Na_2SO_4 concentration.

3.4 Effects of the supporting electrolyte on the hydrogen evolution reaction

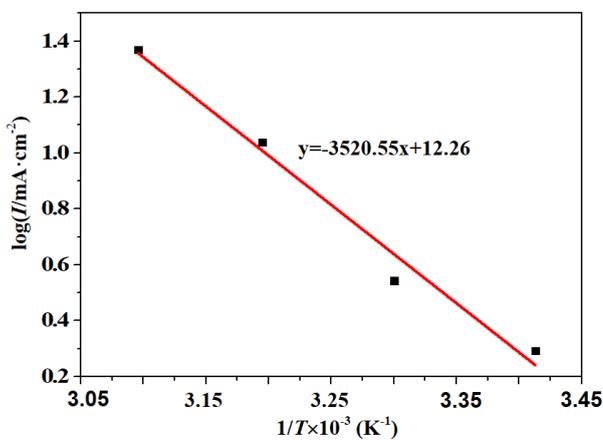
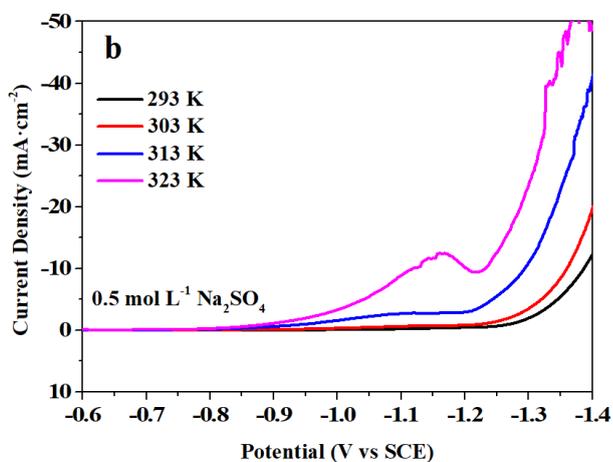
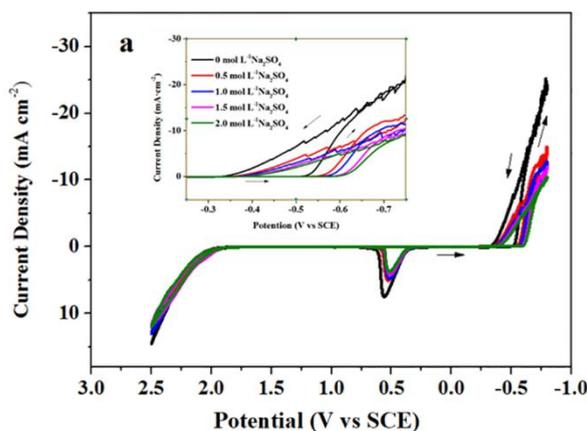
The above studies confirmed the effective role of the supporting electrolyte on Re electrodeposition via 3D microtopography analysis, product composition, current efficiency and galvanostatic discharge study of the Re products. The considerable HER is the most fundamental problem in Re electrodeposition. Therefore, detailed studies of the HER in the presence of the

supporting electrolyte were performed. Fig. 4a shows the CV curves of GCE in solutions with 0.075 mol L⁻¹ NH₄ReO₄, 0.5 mol L⁻¹ H₂SO₄ and different Na₂SO₄ concentrations. The reduction peak of metallic rhenium is not observed because this process is accompanied by intense hydrogen evolution behavior, and excessive hydrogen evolution current masks the reduction peak of rhenium. As the concentration of Na₂SO₄ increases, it can be seen that the onset potential of the HER has a slight negative shift, indicating that the HER is inhibited to a certain extent. Accordingly, after the HER occurs, there is an obvious decline in the reduction current with the increasing of Na₂SO₄ concentration.

Subsequently, a set of linear polarization curves was measured under various temperatures to investigate the activation energy of the HER. Fig. 4b-c represents the polarization curves in solutions with different Na₂SO₄ concentrations and the plots of log*J* versus 1/*T* at the same cathode potential (-1.3 V vs SCE). According to the expression eq. (1), the activation energy of HER can be calculated:

$$\log J = B - E/(2.303R) \times 1/T \quad (1)$$

where *B* is a constant, *E* is the apparent activation energy (kJ mol⁻¹), and *J* is the current density (mA cm⁻²).



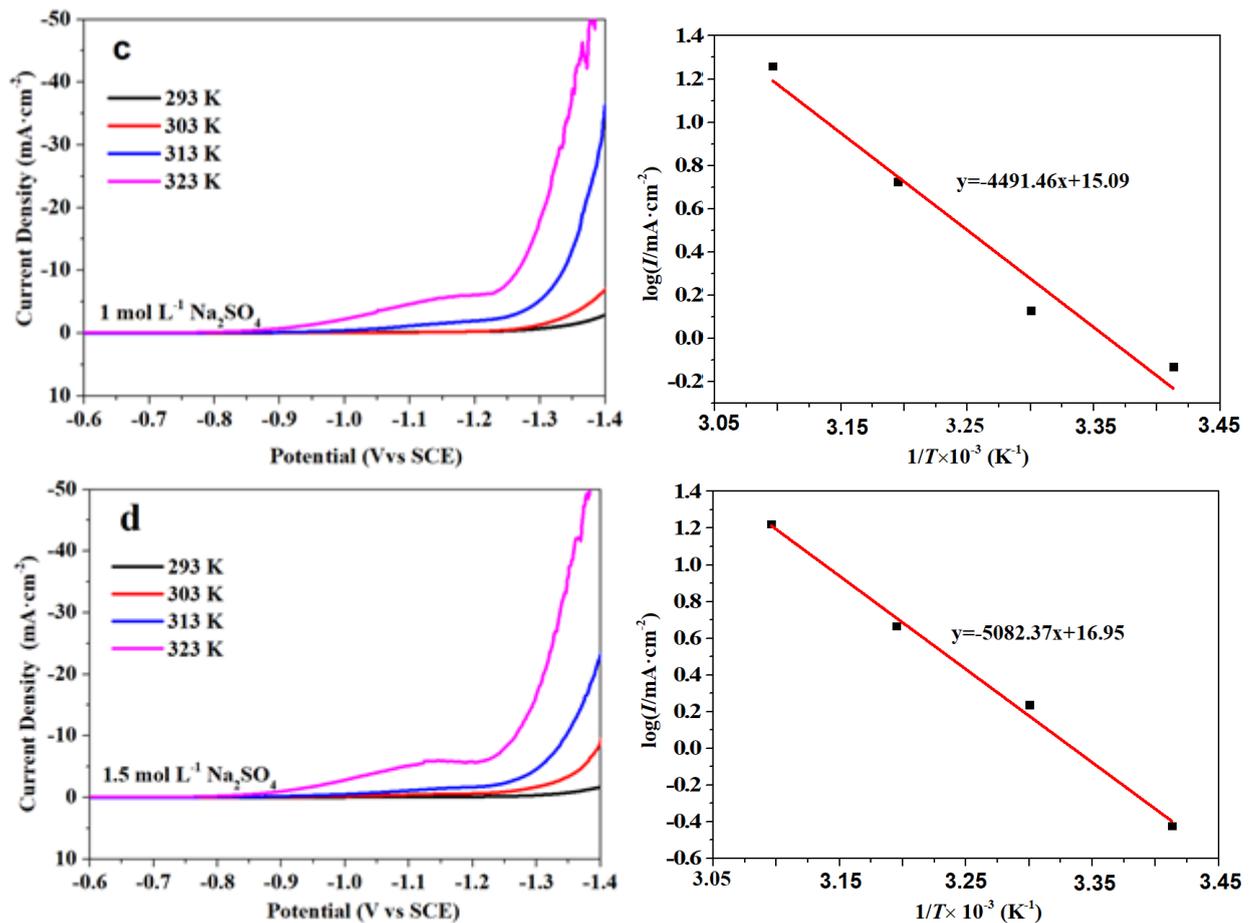


Figure 4. (a) CV curves of GCE in solutions with $0.075 \text{ mol L}^{-1} \text{ NH}_4\text{ReO}_4$, $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and different Na_2SO_4 concentrations, (b-d) polarization curves of GCE in Na_2SO_4 solutions and the corresponding plots of $\log J-1/T$.

The activation energies of the HER in 0.5 , 1 and $1.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solutions are calculated to be 67.32 , 86.00 and $97.31 \text{ kJ mol}^{-1}$, respectively, by the slope of the fitted line of $\log J$ versus $1/T$. This result means that the activation energy of HER can be increased with the increasing of Na_2SO_4 concentration, then the HER side-reaction is reduced. As a result, the addition of Na_2SO_4 facilitates the electrodeposition of metallic Re and improves the current efficiency as evidenced by the electrodeposition experiments and the galvanostatic discharge study.

4. CONCLUSION

Electrolytic metallic rhenium from aqueous solution is always a difficult subject in electrometallurgy due to its low overpotential for the HER. This paper reports an efficient way to electrodeposit metallic rhenium and improve its current efficiency by introducing a supporting electrolyte (Na_2SO_4). The positive effect of the supporting electrolyte on Re electrodeposition was proven by 3D microtopography analysis, product composition, current efficiency and galvanostatic discharge study. Different from the case of lacking the supporting electrolyte, in which only rhenium

oxides can be obtained, herein, under a high concentration of supporting electrolyte, metallic rhenium can be fabricated from more concentrated ammonium perrhenate aqueous solution at a relatively high current efficiency. The introduction of a supporting electrolyte enhances the activation energy of the HER, resulting in the formation of metallic rhenium, and the current efficiency and the surface roughness of the Re products are both improved. The current efficiency reaches 31.4% under optimized conditions, which is far above the values previously reported.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No. 51374185).

References

1. J.C. Carlen and B.D. Bryskin, *Mater. Manuf. Processes*, 9 (1994) 1087.
2. A. Naor, N. Eliaz and E. Gileadi, *Electrochim. Acta*, 54 (2009) 6028.
3. Y.D. Gamburg, A.B. Drovosekov, and T.P. Puryaevam, *Russ. J. Electrochem.*, 51 (2015) 376.
4. P. Antognazza, T. Beringhelli, G. D'Alfonso and A. Minoja, *Organometallics*, 11 (1992) 1777.
5. S. Luidold and H. Antrekowitsch, *JOM*, 59 (2007) 20.
6. M. Bai, Z.H. Liu, L.J. Zhou and C.F. Zhang, *T. Nonferr. Metal Soc.*, 2 (2013) 538.
7. R.L. Mnnheim and J.L. Garin, *Mater. Sci. Forum*, 416-418 (2003) 276.
8. C.G. Fink and P. Deren, *Trans. Electrochem. Soc.*, 1 (1934) 471.
9. Q. Huang and T.W. Lyons, *Electrochem. Commun.*, 93 (2018) 53.
10. E. Salakhova, V. Majidzade, F. Novruzova, P. Kalantarova and R. Huseynova, *J. Chem. Chem. Eng.*, 6 (2012) 489.
11. R. Garcia-Garcia, G. Ortega-Zarzosa, M.E. Rincon and G. Orozco, *Electrocatalysis*, 6 (2014) 263.
12. J.G. Rivera, R. Garcia-Garcia, E. Coutino-Gonzalez, G. Orozco, *Int. J. Hydrogen Energy*, 44 (2019) 27472.
13. Meyer and R. Andre, *Trans. IMF*, 46 (1968) 209.
14. H.Z. Cao, D.G. Chai, L.K. Wu and G.Q. Zheng, *J. Electrochem. Soc.*, 164 (2017) D1.
15. S. Szabo and I. Bakos, *J. Solid State Electrochem.*, 8 (2004) 190.
16. B.P. Hahn, R.A. May and K.J. Stevenson, *Langmuir*, 23 (2007) 10837.
17. L.E. Netherton and M.L. Holt, *J. Electrochem. Soc.*, 95 (1949) 324.
18. R. Schrebler, P. Cury, M. Orellana, H. Gomez, R. Cordova and E.A. Dalchiele, *Electrochim. Acta*, 46 (2001) 4309.
19. C. Morant, L. Galan and J.M. Sanz, *Anal. Chim. Acta*, 297 (1994) 179.
20. M. Komiyama, Y. Ogino, Y. Akai and Goto M, *J. Chem. Soc., Faraday Trans. 2*, 79 (1983) 1719.
21. M.C. Sagiv, N. Eliaz and E. Gileadi, *Electrochim. Acta*, 88 (2013) 240.
22. S. Szabo and I. Bakos, *J. Electroanal. Chem.*, 492 (2000) 103.
23. R. Schrebler, P. Cury, C. Suarez, E. Munoz, F. Vera, R. Cordova, H. Gomez, J.R. Romas-Barrado, D. Leinen and E.A. Dalchiele, *Thin Solid Films*, 483 (2005) 50.
24. A. Vargas-Uscategui, E. Mosquera and L. Cifuentes, *Electrochim. Acta*, 109 (2013) 283.