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Preparation of PtAu Catalytic Particles on Positive Electrode of Li/air Battery Using Pulse Electroplating

Jinqiu Zhang[1,2,*], *Guilin Chen*[1], *Maozhong An*[2], *Peng Wang*[1]

[1] School of Municipal and Environmental Engineering, State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150001, China；
[2] School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, China
[*]E-mail: zhangjinqiu@hit.edu.cn

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To decline the usage of noble metals on air electrode, pulse electrodeposition technology was used to prepare the PtAu catalyst. By Cyclic Voltammograms (CV) test, Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometer (EDS), the optimized bath composition and deposition process were determined as followed: $HAuCl_4$ of 13.3 mmol/L, H_2PtCl_6 of 6.7 mmol/L, H_2SO_4 of 0.5mol/L, peak current density of 100mA/cm^2, pulse width of 5% and frequency of 1kHz. The PtAu catalysts that were prepared under the optimized process distributed on air electrode uniformly with particle sizes of 200~300nm and caused the discharge specific capacity of Li/air battery reaching up to 1300mAh/g$_{carbon+PVDF}$ that was more than two times of that without catalyst.

Keywords: Au-Pt catalyst; pulse electrodeposition; Li/air battery; air electrode

1. INTRODUCTION

Li/air batteries are the possible candidates with high energy densities to meet the need of long-ranged electrified transport. Compared to today’s automotive Li-ion cell whose driving range is limited to about 110 km for a 200 kg pack, Li/air batteries could enable an electric driving range of 610 km on a single charge that is a value approaching that of a gasoline-powered vehicle [1]. However, several challenges need to overcome before the commercialization of Li/air batteries.

The possible reactions involving Li and oxygen depend on the chemical environment and mode of operation, which cause different values of specific energy and energy density of the batteries. In nonaqueous Li/air batteries, there are two principal electrode reactions of interest:

$4Li+O_2\leftrightarrow 2Li_2O$ (1)

$2Li+O_2\leftrightarrow Li_2O_2$ (2)

Abraham and co-workers were the first to report such a successful nonaqueous Li/air cell [2]. The full reduction of oxygen to Li_2O is desired because of its higher specific energy (1794 mAh/g), but it looks that Li_2O_2 with a lower specific energy (1168 mAh/g) is a product that forms more easily than Li_2O [3]. In an aqueous medium, reactions involving Li and O_2 depend on the pH values. In basic aqueous solution O_2 reduction including H_2O results in the formation of soluble LiOH or insoluble $LiOH\cdot H_2O$ that depends on the concentration of LiOH:[4]

$4Li+O_2+2H_2O\leftrightarrow 4LiOH$ (3)

$LiOH+H_2O\rightarrow LiOH\cdot H_2O$ (4)

The oxygen reduction reaction (ORR) during discharge and oxygen evolution reaction (OER) during charge are taken place on porous air electrode sluggishly in Li^+-containing aprotic electrolytes without catalyst [5], which influence the properties of the Li/air battery significantly. In order to increase the specific capacity and decrease the charge voltage of the Li/air battery, catalysts should be used to accelerate the ORR and OER [6]. Excellent catalytic activity and stability in the electrolyte are the requirements for the catalyst of ORR and OER. Noble metals and alloys [7] and transition metal oxide [8, 9] were used as catalysts on air electrode in published reports. Debart et al. studied the effect of several catalysts on the properties of Li/air batteries and found that catalysts have little effect on discharge voltages, but have significant effect on specific capacities, charge voltages and cyclic properties. Catalysts composed by nano particles are better for ORR and OER due to their large surface area compared to bulk ones [10]. By use of α-MnO_2 nanowires catalyst, the capacity of Li/air cell reaches to 3000 mAh/g of carbon. In the work of Lu et al. [11], Au-Pt nano particles mixed in the electrode active material are successful bi-functional catalysts where Au particles and Pt particles target ORR and OER, respectively. Au-Pt nano particles show the highest round-trip efficiency of ~77% up to now and get attention again despite of the high cost of noble metals.

Compared with mixing catalyst in the slurry, the pulse electroplating technology [12] could prepare thickness controlled and small sized metallic catalyst on electrodes. In this paper, we studied the effect of pulse electroplating parameters and bath compositions on the catalytic properties of PtAu particles on carbon electrodes.

2. EXPERIMENTAL

2.1 Pulse electroplating of PtAu particles

0.75g of polyvinylidene fluoride (PVDF, AR) is dissolved in 3.0g of N-methyl pyrrolydone (NMP, AR). 0.25g of acetylene black was added to the PVDF/NMP mixture and blended by a magnetic rotor for 12h. Porous air electrodes were used as cathodes that were prepared by loading the Carbon/PVDF/NMP slurry on nickel foam (thickness of 1.8 mm, Changsha Liyuan new meterials Co. Ltd.) sheets and then drying for 12h. A gold plate was used as anode. Baths of 50 ℃ contained $HAuCl_4$ of 6.7~13.3 mmol/L, $H_2Pt\ Cl_6$ of 6.7 ~13.3 mmol/L and H_2SO_4 of 0.5mol/L. Pulse electroplating were carried 60s for one piece of cathode by a pulse power (DMC-30M, Shenzhen Yuanshunda Electronic Machinery Co., Ltd.) with parameters adjusting as peak current density of 100~250mA/cm^2, pulse width of 5%~30% and frequency of 0.1~1kHz.

2.2 Assembly of Li/air cell

CR2025 coin cells with 1mm diameter holes on top-cover were used to assemble nonaqueous Li/air cell in a glove box full of argon. Positive electrodes were porous air electrodes with or without PtAu catalysts. Negative electrodes were lithium disk slices of 14mm diameter. Polypropylene membranes (thickness of 20μm, Celgard) were dipped in an ionic liquid electrolyte prepared by adding Li-TFSI into EMI-TFSI liquids and agitating for 6~8h, and then assembled in the cells, where TFSI means Tri Fluoro methyl Sulfonyl Imide, EMI means 1-Ethyl-3-MethylImidazolium.

2.3 Measurements

Stability of PtAu catalyst were characterized by cyclic voltammetric (CV) measurements using an electrochemical analyzer (CHI630B, CH Instruments) at scan rate of 10mV/s in 1mol/L KOH aqueous solutions that were aerated with oxygen of 20 min[13]. PtAu alloy coatings were pulse electrodeposited on Glassy Carbon (GC) electrodes (geometric area: 0.2 cm^2) polished by 1.5μm α-Al_2O_3, which were used as working electrodes. Hg/HgO electrode and Platinum plate of 1cm^2 were reference electrode and counter electrode, respectively. Morphologies and compositions of PtAu catalyst were measured by scan electron microscopy (SEM) and energy-dispersive X-ray (EDX), respectively. Charge and discharge behaviors of Li/air cells were tested in air atmosphere using battery test system (Neware CT-3008W) at constant current (CC) steps of 0.05 mA/cm^2 in voltage range of 1.8V~4.0V vs. Li/Li$^+$ at ambient temperature (25±2 ◦C).

3. RESULTS AND DISCUSSION

3.1 Effect of pulse electroplating parameters on catalytic property of PtAu particles

Polished GC electrodes with uniform surfaces were used as substrate to evaluate the effect of pulse electroplating parameters on catalytic activities of PtAu catalysts. As shown in Fig.1a, the large wave at about 0.17V (vs. Hg/HgO, the same below) during negative direction scanning suggests the reduction of absorption oxygen or oxides, and the increase of current from 0.35V to 0.7V suggests the evolution of oxygen during positive direction scanning [14]. The peak current of 0.006mA at about 0.17V in fig.1a’ is less than that of 0.011mA in fig.1a, which indicates that the activity and stability of

PtAu catalyst particles decrease after long time usage. However, there are not similar waves in fig.1c, which shows that PtAu coating has clear catalytic activity on oxygen and GC has not effect on catalyst evaluation.

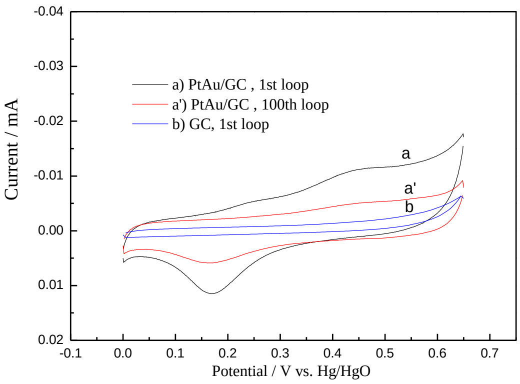

Figure 1. a) The 1st and a') the 100th CV loops of PtAu coating pulse electrodeposited on GC electrodes from a bath containing $HAuCl_4$ of 10 mmol/L, H_2PtCl_6 of 10 mmol/L and H_2SO_4 of 0.5mol/L at peak current density of 150 mA/cm^2, pulse width of 10% and frequency of 100Hz, and b) the first CV loop of GC electrodes in O_2-saturated 1 mol/L KOH solution

As shown in Fig.2a, with the increase of peak current densities from 100 to 250 mA/cm^2, the peak current values at about 0.17 V decrease from 0.014 to 0.01 mA. After 100 times circulation as shown in Fig.2b, the peak current values at about 0.17 V also decrease in which that deposited at 100 mA/cm^2 remains the biggest value of 0.006mA. Obviously, the activity and stability of the coating obtained at 100mA/cm^2 are better than that of others, which maybe is influenced by the proper compositions and morphologies of PtAu coating obtained at a lower peak current density.

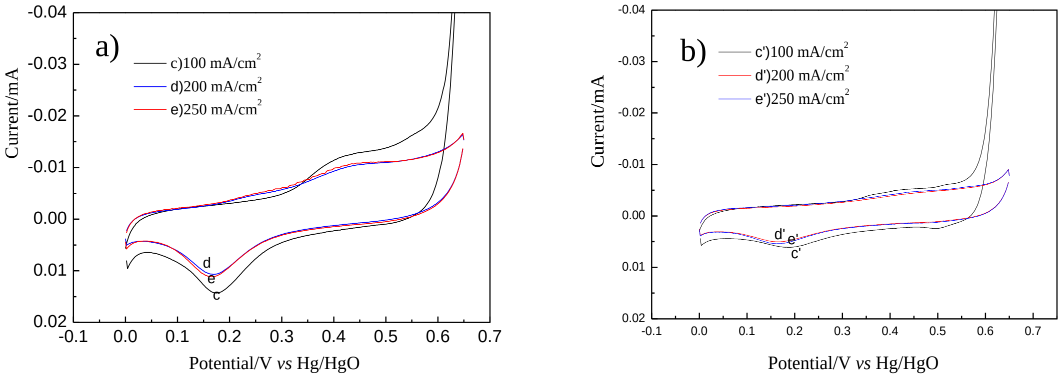

Figure 2. In O_2-saturated 1 mol/L KOH solution a) the 1st and b)the 100th CV loops of PtAu coatings pulse electrodeposited from a bath containing $HAuCl_4$ of 10 mmol/L, H_2PtCl_6 of 10 mmol/L and H_2SO_4 of 0.5mol/L at different peak current densities, pulse width of 10% and frequency of 100Hz.

Fig.3 shows that the PtAu coating deposited at pulse width of 5% has a better catalytic activity and stability, which the peak current at about 0.19V in 1st and 100th loop are 0.015 mA and 0.006mA . Pulse width is a pulse on-time percentage of a total pulse period.

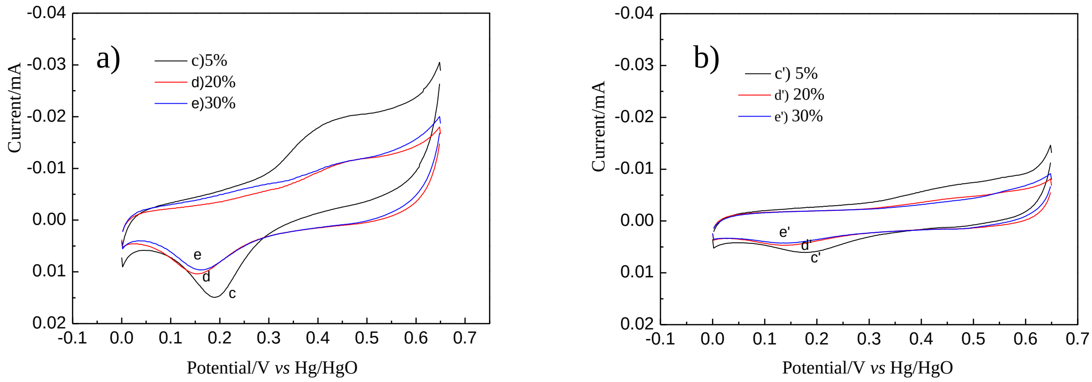

Figure 3. In O_2-saturated 1 mol/L KOH solution a) the 1st and b)the 100th CV loops of PtAu coatings pulse electrodeposited from a bath containing $HAuCl_4$ of 10 mmol/L, H_2PtCl_6 of 10 mmol/L and H_2SO_4 of 0.5mol/L at peak current densities of 150mA/cm^2, different pulse width and frequency of 100Hz.

In the 1st loop of CVs as shown in Fig.4a, the peak current values at about 0.18V are proportional to the pulse frequencies. The catalytic activities of PtAu coatings increase significantly with elevated pulse frequencies. When the pulse frequent is 1000Hz, the peak current reaches to 0.019mA in the first CV loop (Fig.4a-c). In general, elevated pulse frequency is good to decrease the concentration polarization and fine the crystal grains that increase the specific surface area of the catalyst coating and improve the catalytic activity [15]. Thus, a faster pulse frequency is better for the deposition of the catalyst coating with a higher activity.

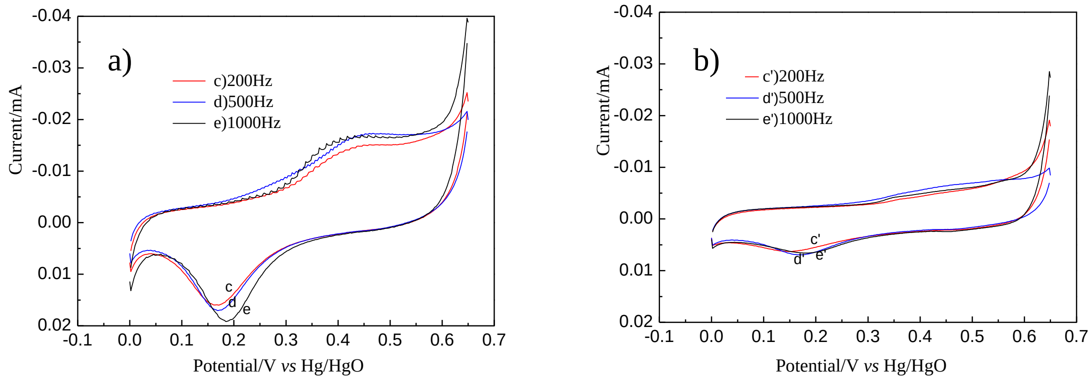

Figure 4. In O_2-saturated 1 mol/L KOH solution a) the 1st and b)the 100th CV loops of PtAu coatings pulse electrodeposited from a bath containing $HAuCl_4$ of 10 mmol/L, H_2PtCl_6 of 10 mmol/L and H_2SO_4 of 0.5mol/L at peak current densities of 150mA/cm^2, pulse width of 10% and different frequency.

When the pulse width increases, the consumed quantity of metal ions also increases. However, the metal ions have not enough time to migrate from the bulk solution to the electrode surface, which causes a larger concentration polarization and bigger size particles [16]. So, a smaller pulse width is better for the formation and the growth of smaller size particles.

3.2 Effect of bath compositions on properties of PtAu particles

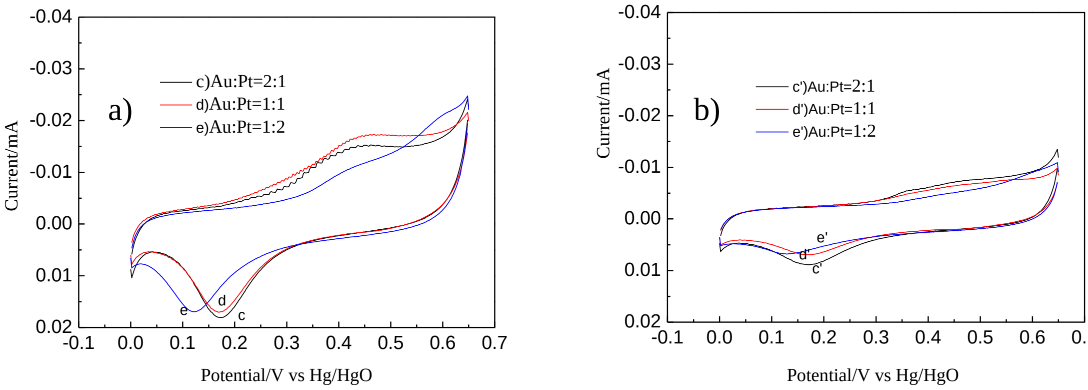

Figure 5. In O_2-saturated 1 mol/L KOH solution a) the 1st and b)the 100th CV loops of PtAu coatings pulse electrodeposited at peak current densities of $100mA/cm^2$, pulse width of 5% and pulse frequency of 1kHz form bath containing c) and c') $HAuCl_4$ 13.3 mmol/L+ $H_2Pt\ Cl_6$ 6.7 mmol/L+H_2SO_4 0.5mol/L, d)and d') $HAuCl_4$ 10 mmol/L+ $H_2Pt\ Cl_6$ 10 mmol/L+H_2SO_4 0.5mol/L, and e) and e') $HAuCl_4$ 6.7 mmol/L+ $H_2Pt\ Cl_6$ 13.3 mmol/L+H_2SO_4 0.5mol/L.

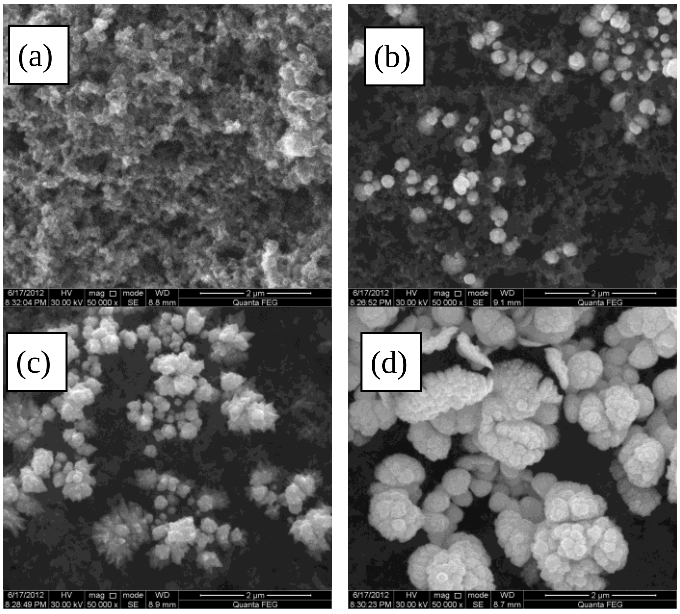

Figure 6. SEM images of the air electrodes a) without pulse electrodeposition, b), c) and d) pulse electrodeposited at peak current densities of $100mA/cm^2$, pulse width of 5% and pulse frequency of 1kHz form bath containing $HAuCl_4$ 13.3 mmol/L+ $H_2Pt\ Cl_6$ 6.7 mmol/L+H_2SO_4 0.5mol/L, $HAuCl_4$ 10 mmol/L+ $H_2Pt\ Cl_6$ 10 mmol/L +H_2SO_4 0.5mol/L, and $HAuCl_4$ 6.7 mmol/L+ $H_2Pt\ Cl_6$ 13.3 mmol/L+H_2SO_4 0.5mol/L, respecitively.

With the ratios of concentrations of $HAuCl_4$ and $HPtCl_6$ in the baths change, the peak current values and positions are different. When the mole ratio of Au: Pt in the bath is 2:1, the PtAu coating has the highest peak currents in Fig.5a and Fig.5b that are 0.018 and 0.009mA, respectively, which indicates that with the elevated ratios of Au in the bath, the catalytic activities of the PtAu coating increase. As shown in Fig.6, different bath compositions also lead to different morphologies of PtAu particles. Compared to the air electrode without pulse electroplating (Fig.6a), the white particles with various shapes shown in Fig. 6b, Fig. 6c and Fig. 6d are PtAu catalysts. When the mole ratio of Au: Pt in the bath is 2:1, the PtAu particles are uniformly deposited on the air electrode with the smallest sizes of 200~300nm and the mass content ratio of Pt: Au in the deposits is 57:43, which is nearly 1:1 that is consistent with the reference report that 50%Pt-50%Au alloy has the best catalyst activity [11].

3.3 Charge/discharge property of Lithium-air batteries

Compared the first cycle charge/discharge curves of Li/air batteries using different air electrodes as shown in Fig. 6, it is found that the Li/air battery using carbon electrode with PtAu particles catalyst has better performance than that without catalyst. The discharge and charge platforms of the Li/air battery using carbon electrode with PtAu particles catalyst are about 2.1V (vs. Li/Li^+, the same below) and 3.6V, respectively, where the discharge and charge voltages of the cell are all lower than that reported in the references [11, 17]. However, the Li/air battery using carbon electrode without catalyst has not clear the discharge and charge platforms. Furthermore, the discharge specific capacity of the Li/air battery using PtAu catalyst is 1150 $mAh/g_{carbon+PVDF}$, which is obviously more than that of the Li/air battery without catalyst of 520 $mAh/g_{carbon+PVDF}$. By use of the PtAu catalyst particles pulse electrodeposited from the bath containing $HAuCl_4$ of 13.3 mmol/L and H_2PtCl_6 of 6.7 mmol/L, the discharge specific capacity of the Li/air battery increases to 1300$mAh/g_{carbon+PVDF}$, which shows that it is a better catalyst that is coincident with the results in section 3.2.

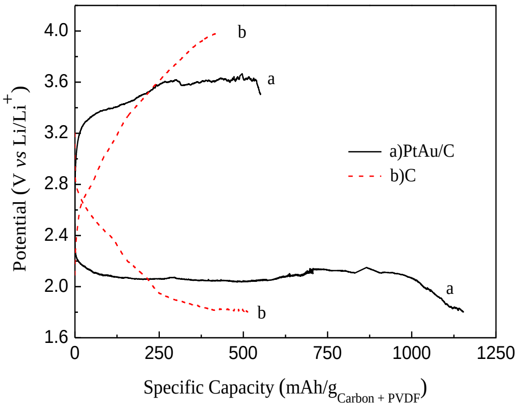

Figure 7. The first cycle charge/discharge curves of Li/air batteries using carbon air electrode a) without catalyst and b) with PtAu particles pulse electrodeposited at peak current densities of 100mA/cm^2, pulse width of 5% and pulse frequency of 1kHz from bath containing $HAuCl_4$ 10 mmol/L+ H_2PtCl_6 10 mmol/L+H_2SO_4 0.5mol/L.

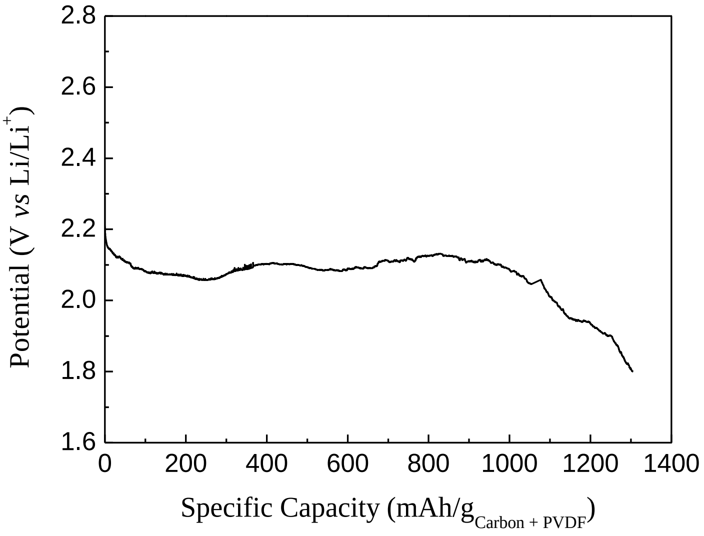

Figure 8. The first cycle discharge curve of Li/air batteries using carbon air electrode with PtAu particles pulse electrodeposited at peak current densities of 100mA/cm^2, pulse width of 5% and pulse frequency of 1kHz from bath containing $HAuCl_4$ 13.3 mmol/L+ H_2Pt Cl_6 6.7 mmol/L+H_2SO_4 0.5mol/L.

Unfortunately, the charge and reversible properties of these Li/air batteries are not as good as their discharge properties. The corrosion of Li negative electrode, the decomposition of electrolyte and the produce of irreversible electrode products are the possible reasons and also the challenges to be overcome in the future [17].

4. CONCLUSIONS

PtAu catalyst particles were pulse electrodeposited on carbon air electrodes and that were assembled in Li/air batteries. In conclusion, the PtAu particles pulse electrodeposited on surface of carbon air electrodes have catalytic activities for the ORR and OER, which also decrease the cost of noble metals. The optimized pulse electroplating process and bath composition to get better catalytic PtAu particles are peak current densities of 100mA/cm^2, pulse width of 5%, pulse frequency of 1kHz, and bath containing $HAuCl_4$ of 13.3 mmol/L, H_2Pt Cl_6 of 6.7 mmol/L, and H_2SO_4 of 0.5mol/L. By use of the PtAu particles that deposited at above parameters, the discharge specific capacity of the Li/air battery reaches to 1300mAh/g$_{\mathrm{carbon+PVDF}}$. The future work will focus on preparation of morphology-controlled PtAu particles for better catalytic performance by pulse electroplating.

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References

1. J Christensen, P Albertus, Rs Sanchez-Carrera, T Lohmann, B Kozinsky, R Liedtke, J Ahmed and A Kojic, *J Electrochemical Society*, , 159 (2012) R1
2. K M Abraham and Z Jiang, *J Electrochemical Society*, 143(1996) 1
3. G Girishkumar, B Mccloskey, A Luntz, S Swanson and W Wilcke, *J Physical Chemistry Letters*, 1(2010) 2193
4. P Gierszewski, P Finn and D Kirk, *Fusion Engineering and Design*, 13(1990) 59
5. D Aurbach, M Daroux, P Faguy and E Yeager, *J Electroanalytical Chemistry*, 297(1991) 225
6. J Suntivich, H A Gasteiger, N Yabuuchi, H Nakanishi, J B Goodenough and S H Yang, *Nature Chemistry* , 3(2011) 546
7. A Tegou, S Papadimitriou, S Armyanov, E Valova, G Kokkinidis and S Sotiropoulos, *J Electroanalytical Chemistry*, 623(2008) 187
8. T Ogasawara, A Débart, M Holzapfel, P Novák and P G Bruce, *J American Chemical Society*, 128(2006) 1390
9. H L Wang, Y Yang, Y Y Liang, G Y Zheng, Y G Li, Y Cui and H J Dai, *Energy & Environmental Science*, 5(2012) 7931
10. A Débart, A J Paterson, J Bao and P G Bruce, *Angewandte Chemie*. 120(2008) 4597
11. Y C Lu, Z C Xu, H A Gasteiger, S Chen, K Hamad-Schifferli and S H Yang, *Journal of the Ameirican Chemical Society*, 132(2010) 12170
12. H S Kim, N P Subramanian and B N Popov, *J Power Sources*. 138(2004)14
13. J Ma, X Wang and X Jiao, *Int. J. Electrochem. Sci.*, 7 (2012) 1556
14. B Unnikrishnan, Y Umasankar, S Chen and C C Ti, *Int. J. Electrochem. Sci.*, 7 (2012) 3047
15. F Xiao and Y Xu, *Int. J. Electrochem. Sci*., 7 (2012) 7440
16. C N Su, M Z An, P X Yang, H W Gu and X H Guo, *Applied Surf. Sci.* 256 (2010) 4888
17. H G Jung, J Hasssoun, J B Park, Y K Sun and B Scrosati, *Nature Chemistry*, 4(2012)579