Magneto-electrodeposition AuPt paticles on carbon paper as cathodic catalyst of lithium air battery

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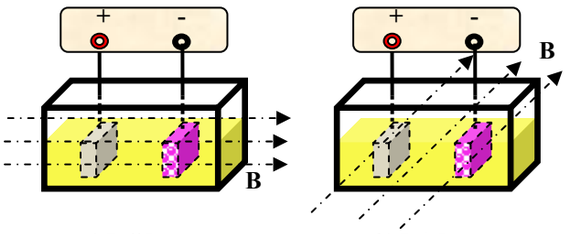
The first lithium air battery was successfully assembled and discharged by K.M. Abraham et al. in 1996 [1]. In a lithium air battery, an oxygen electrode and a piece of lithium plate are used as cathode and anode, respectively. Catalysts are usually loaded on porous carbon cathode to accelerate Oxygen Reduction Reaction (ORR) and Oxygen Evolution Reaction (OER). However, most catalysts, such as α-MnO_2 or single noble metal, only have good catalytic actions on ORR, not OER. So, bi-functional catalysts are developed [2]. $Pt_{0.5}Au_{0.5}$ nano particles exhibit good bifunctional catalytic activity [3]. In this paper, magneto-electrodeposition was carried to in-situ load AuPt particles on carbon paper, and the effect of magnetic field parameters and pulse deposition parameters on properties of catalyst were studied.

Electrodeposition cell was set in a static magnetic field generated by two pieces of rubidium–iron–boron magnets (78mm×57mm×17mm, Shanghai Yan-Tai metal materials Co., Ltd). B//J is defined as magnetic field oriented parallel to electric field (Fig.1a), while B⊥J is defined as magnetic field oriented vertical to electric field (Fig. 1b). Magnetic flux density of the magnetic field was range from 40mT to 220mT by adjusting the distance of two pieces of magnets.



a) B // J b) B⊥J

Fig 1 Sketch of the magnetic field a) B//J oriented parallel to electric field and b) B⊥J oriented vertical to electric field.

Electrodeposition baths of 25℃ contained $HAuCl_4$ of 6.7~13.3 mmol/L, H_2PtCl_6 of 6.7~13.3 mmol/L and H_2SO_4 of 0.5mol/L. AuPt particles were pulse electrodeposited on carbon paper (15mm×15mm×0.3mm, Toray Industries, Inc.) by Recurrent Galvanic Pulses – 2 Galvanic Pulse model using PARSTAT 2273 with parameters as current density of 20~364mA/cm^2, pulse width of 10%~50%, frequency of 0.04~1kHz and total quantity of electricity of 2C. A gold plate was used as anode. A L25(5^6) orthogonal experiment design method was used and evaluated by activity area of AuPt catalysts. Activity areas were calculated by integral area of hydrogen adsorption peaks in cyclic voltammetry (CV) that were measured using PARSTAT 2273 (Fig.2). Parts of orthogonal experimental data were listed in Table 1. It was found that the order of significant factors for AuPt catalyst is pulse width> current density > pulse frequency > magnetic field direction > concentration ratio of gold salt to platinum salt > magnetic flux density. The magnetic field direction of B⊥J has positive effect on improvement of activity area of AuPt catalyst because Magnetohydrodynamic (MHD) influence caused by Lorentz force accelerates formation of new grains.

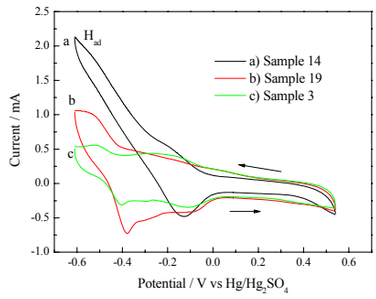


Fig.2 CVs of AuPt/C a) Sample14, b) Sample 19 and c)Sample 3 measured at scan rate of 50mV/s in 0.1mol/L $HClO_4$ aqueous solutions that were aerated with Argon of 20 min.

Table 1 Parts of orthogonal experimental data

Sample No.	3	14	19
Pulse width/%	30	10	20
Current Density/mA·cm^{-2}	100	200	200
Pulse frequency/KHz	0.2	0.2	1
Magnetic field direction	Blank	B⊥J	B // J
$[HAuCl_4]$:$[H_2PtCl_6]$	1:1	3:1	1:1
Magnetic flux density/mT	220	110	80
Activity area/m^2·g^{-1}	2.32	9.47	3.93

Compare the micro morphologies of AuPt catalysts on carbon paper in Fig.3 with their activity area, it shows that smaller particles have bigger activity area, which were usually pulse electrodeposited under smaller pulse width and frequency, bigger current density and B⊥J. The magnetic flux density and the concentration ratio of gold salt to platinum salt have little influence on activity area. The optimized pulse electrodeposition parameters are pulse width of 10%, pulse frequency of 0.04KHz and current density of 200 mA·cm^{-2}. The future work will focus on the effect of each pulse electrodeposition parameter on properties of AuPt particles and AuPt/C electrode in lithium air batteries.

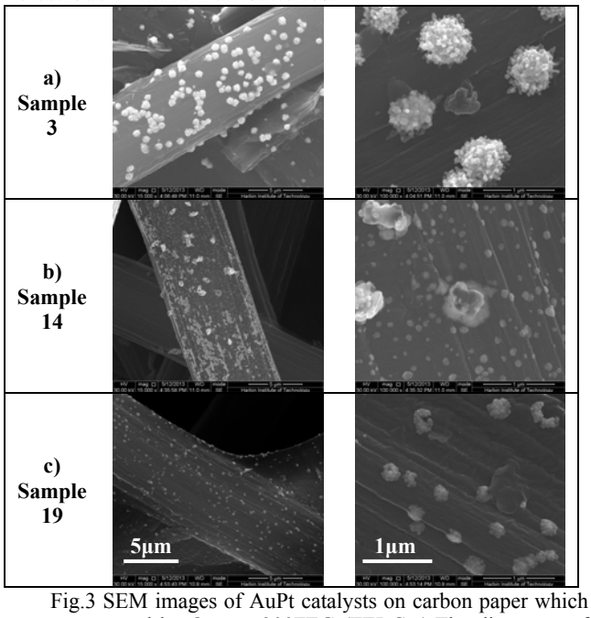


Fig.3 SEM images of AuPt catalysts on carbon paper which were measured by Quanta 200FEG (FEI Co.).The diameters of AuPt particles are in range of a) 590~740nm, b) 37~150nm and c) 220~350nm.

References

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