DECHEMA FORSCHUNGSINSTITUT

Chemical Technology

Corrosion test of different carbons in 7M KOH for electrically rechargeable metal/air batteries

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Introduction /Objectives

Numerous carbon blacks have already been investigated and used in several electrochemical applications because of their excellent electronic conductivity. However their utilization is limited by poor corrosion resistance, especially as cathode material at high potential value and in highly concentrated alkaline electrolytes. This work aimed at testing six different commercial carbons (C65, C45, Ketjen Black, Vulcan carbon black; HSAG high surface area graphite and KS6L graphite) by electrochemical and thermal stability methods and selecting the most stable one as additive for bifunctional perovskite catalyst in a rechargeable Metal/Air Battery.

Background

Fig. 1: (A) Photo of a Zn/Air button cell. (B) Scheme of a Metal/Air Battery. Below: electrode reactions in alkaline Al/air cell

Al/Luft[1]

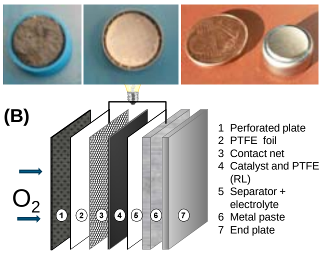
Anode: $4Al + 16OH \rightarrow 4Al(OH)_4 + 12e$

$2Al + 2OH^- + 6H_2O \rightarrow 2Al(OH)_4^- + 3H_2$

Kathode: $3O_2 + 6H_2O + 12e \rightarrow 12OH$

Gesamt: $4Al + 3O_2 + 6H_2O + 4OH^- \rightarrow 4Al(OH)_4^-$

$Al(OH)_4^- \rightarrow Al(OH)_3 + OH^-$



➢ Metal/air batteries possess high theoretical energy density (Al: 21.994 Wh/L Zn 1300 Wh/L; Si: 19.800 Wh/L) and raw materials are cheap and relatively abundant.

Carbon properties

Carbon material should increase electrode conductivity, be corrosion-resistant, prevent flooding, have high capacitance for possible reaction products, promote oxygen transport, possess high surface area and avoid electrode collapsing.

Carbon	Size [nm]	BET [m²/g]	Loading [µg]
Ketjen Black	34	1325	130
HSAG 300	30.000	280	110
Vulcan	50	250	120
C65	35	62	140
KS6L	3.200	20	160
C45	--	45	180

Table 1: Specifications and loading mass of tested commercial carbons: KB (Akzo Nobel), VulcanXC72R (Cabot), HSAG, C65, C45 & KS6L (TIMCAL)

➢ Carbon blacks Vulcan and C45 have the smallest bulk density of 0,079 g/cm³, followed by C65 with 0,11 g/cm³, and 0,14 g/cm³ for KB. KS6L and HSAG graphitized carbon possesses the biggest bulk density of 0,40 g/cm³ and 0,42 g/cm³.

Fig.2: Volume evaluation of 1g of each carbon in Ø11,3 cm tubes.

Ink preparation and electrode coating

➢ Typical ink composition: 10 mg carbon + 10 wt% Nafion in 1,5 g isopropanol + 1g water.

➢ ∅24,75 mm² of the glassy carbon electrode was coated with 3µl of the prepared suspension in an interval of 10 – 20 min till area of the glassy carbon electrode was completely covered by carbon particles (see Fig 2(A)).

➢ For electrochemical investigations, carbon-coated electrode was placed into a half-cell filled with 7M KOH as electrolyte, Pt as counter- and Hg/HgO as reference electrode (see Fig 2(B))

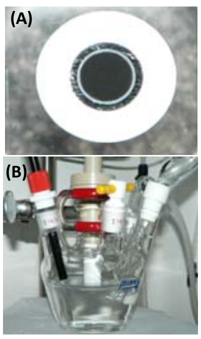


Fig.2: (A) Carbon-coated Glassy Carbon (GC) disc working electrode with Pt ring. (B) 3-Electrode electrochemical cell used for electrochemical corrosion investigations.

Electrochemical investigation protocol

Procedure	Potential range [mV]	dE/dt [mV/s]
Start and end CV	-1300 – +250	40 and 5
ADT	-1350 – +250	1000
Control CV	-1750 – +600	40

Table.2: Potential range and potential scan rate of different cyclic voltammogramms (CV) protocols used during stability tests.

Accelerated Degradation Tests (ADT)

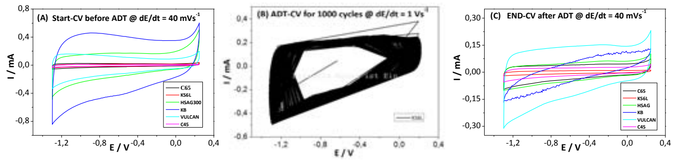


Fig.3: (A) Cyclic voltammogramms (CV) of different carbons before ADT. (B) Typical CV behavior of KS6L during 1000 cycles at 1V/s. (C) CV of the same carbons after ADT procedure in 7 M KOH and RT.

➢ Before ADT, C45 exhibits smallest double layer capacity (C_D) value, KB and HSAG300 the largest ones but after ADT the latter ones decreased dramatically.

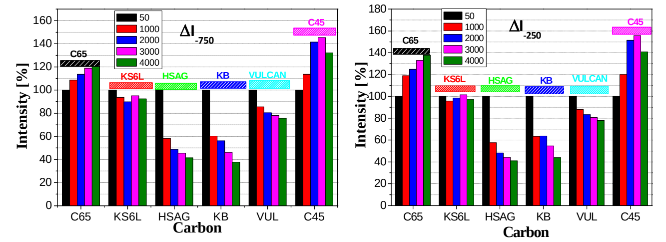


Fig.4: Summary of C_D current values in function of cycle number at -750 & -250mV from control CV at 40mV/s in 7 M KOH.

➢ Most stable carbon systems are KS6L and Vulcan with a decrease of 7,5% and 25% at ΔI-750 and 2% and 22,6% at ΔI-250, respectively after 4000 cycles.

➢ C65 and C45 show surprisingly an increase in C_D of 23% and 32% at ΔI-750 and 38% and 41% at ΔI-250, respectively after 4000 cycles.

Determination of carbon double layer capacity

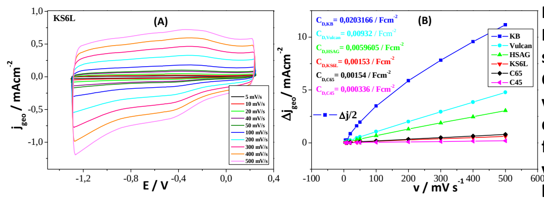


Fig.5: (A) CVs of KS6L at different scan rates. (B) Calculated CD values of the different carbons from slope of Δj/2 vs. scan rate in linear region extracted from E/j plots @ -300mV.

Carbon	Loading-normed BET [cm²]	C_D [F]	$C_{D,loading}$ [F/g]	$C_{D,BET}$ [F/cm²]
C65	68,2	3,8E-4	3,47	5,59E-6
KS6L	32	3,79E-4	2,38	1,18E-5
C45	81	8,32E-5	0,46	1,03E-6
KB	1457,5	5,03E-3	45,70	3,45E-6
HSAG	392	1,48E-2	10,54	3,76E-5
VULCAN	375	2,32E-3	15,49	6,20E-6

Table 3: Listed CDs as well as loading- and BET-normalized C_D values .

➢ The larger the BET surface, the highest the $C_{D,loading}$ value.

Thermogravimetrical analysis (TGA)

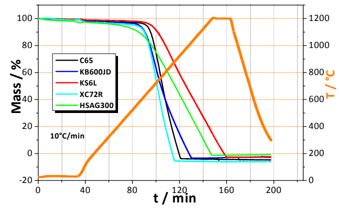


Fig.6: TGA behavior of different carbons in Ar.

➢ Thermal stability of the carbons increases in the following sequence: HSAG300 < Vulcan XC72R ≈ KB600JD < C65 < KS6L.

➢ This behavior correlates partially with electrochemical investigations.

Summary and outlook

➢ From all investigated carbons, KS6L was the most stable system during both electrochemical (EC) and TGA investigations, followed by Vulcan (EC) & C65 (TGA).

➢ Next step, investigating on the electrochemical and thermal Stability of catalyst-Carbon mixtures in different weight percent under the same conditions (ie: 7M KOH at RT).

➢ For technical application we had to choose among all analyzed materials a graphite carbon (KS6L) and a carbon black (Vulcan XC72R).

Acknowledgements

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