

Study on Fe-doped Activation Carbon-based Supercapacitor at 4V

Jie Li, Zhou Xu*, Zhian Zhang*

School of Metallurgy and Environment, Central South University, Changsha 410083, China.

*E-mail: csuxuzhou@163.com, zxa75@163.com

Received: 9 April 2019 / *Accepted:* 3 July 2019 / *Published:* 31 July 2019

Iron impurities will be mixed into the products during the production of supercapacitors due to wear and tear of equipment. So, this paper designs a Supercapacitor system of Fe-doped activated carbon, in a pouch scale, is studied with the use of organic electrolyte (salt of $\text{MeEt}_3\text{NBF}_4$ in the solvent of propylene carbonate) at 4V. Gas evolution, from the decomposition of electrode, electrolyte and the binders (sodium carboxymethyl cellulose and polymerized styrene butadiene rubber) is in situ analyzed with the simultaneous analysis of electrochemical signals, when the pouch of supercapacitor was integrated with a gas bag. The addition of Fe on activated carbon results in the production of H_2 , CO and CO_2 as the dominant gases with the accelerated rate, while no CO and CO_2 are produced in the absence of Fe. The determination of the origin of gases suggests that salt of $\text{MeEt}_3\text{NBF}_4$ of electrolyte is firstly decomposed in the absence of Fe. While sodium carboxymethyl cellulose is firstly decomposed in the presence of Fe, due to its hydrophilic property and the structure of electrode sheet. A mode of gas evolution was established as considering processing technology and the hydrophilic properties of materials. The results provide a new insight on the “buckets effect” of supercapacitor that the metal impurities, exhibit much serious negative effect in decomposing components inside device, not limited to the decomposition of electrolyte as previously reported.

Keywords: Supercapacitor; Activated carbon; Organic electrolyte; Gas evolution; High voltage

1. INTRODUCTION

Supercapacitor (SC), an important device for electrochemical energy storage, exhibited high power density, extra-long cycling stability and had wide potential applications in cold start-up of vehicles, power backup and the recycled use of energy in braking [1-4]. Actually, the commercialized SC (with the electrode of activated carbon (AC) and organic electrolyte) operated at 2.7V had cycling stability more than several hundred thousand times. However, it is well known that SC had the lower energy density, compared to Pb-acid battery and Li-ion battery, which limited their application field seriously. Elevation of the operating voltage of the SC is effective to increase the energy density of SC,

considering the energy density of SC increased with two orders of operating voltage. One effort is to use new electrodes (carbon nanotube and graphene) with intrinsic structural stability at high voltage [5-7]. Another effort is to decrease the content of impurities in the conventional AC based SC system as far as possible [5,8]. Actually, the presence of impurities including water, metal, oxygen-, nitrogen-, or other functional groups on AC [1,9,10] and other carbon materials resulted in the decomposition of electrolyte or other components of SC at 2.7V. For instance, for a SC system with organic electrolyte with propene carbonate (PC) as solvent and the electrode of AC with oxygen containing groups in large amounts, CO and propene was the dominant product of gases in the decomposition process [11-14]. Origin of propene was attributed to the decomposition of PC. But the origin of CO was not so clear for a long time. On the other hand, as the purity of AC was improved by the multiple treatment with acids or bases, hydrogenation in high temperature or high temperature evaporation under vacuum [15-16], the gas analysis presented different results [17]. The result suggested the gas information is impurities dependent, stressing the necessity of revisiting the metal impurities effect on the stability of components in SC as operated in high voltage.

Herein, a commercial AC with high purity was intentionally doped with Fe to understand the effect of Fe impurities of AC on the stability of any components inside SC at 4V. The gas evolution in organic electrolyte (PC- MeEt₃NBF₄ and binder of polymerized styrene butadiene rubber (SBR) and sodium carboxymethyl cellulose (CMC) was *in situ* studied with a combined system of gas analysis and electrochemical signal detection. In addition, the operating voltage is adopted to be 4 V, which mimics the state of accelerating aging in catalytic process, considering the life time of SC is too long to be measure if operated in a mild condition. It, for the first time, is found that H₂ and hydrocarbons (C₁-C₃) were the main products and CO, CO₂ was absent if using AC without containing Fe in large amount. However, the intentional doping of Fe (0.05%-0.2 %) on AC resulted in the production of CO and CO₂ in large amount. And H₂, CO and CO₂ were the main gas product. In addition, the addition of Fe resulted in the sustainable production of gases in relatively large amount, different from the case without Fe. The combined analysis of the components and the volume of gases suggested that the addition of Fe resulted in the decomposition of CMC and salt in advance. However, the decomposition of salt is the main route in the case of without Fe in large amount. As a result, a mode of the decomposition of the component of SC was established, considering the processing technology of the electrode and the hydrophilic or hydrophobic properties of the components. These results provide the deep insight on the combination of metal (to provide pseudo-capacitance) and the development of associated salt and binder in the future.

2. EXPERIMENTAL

2.1. The doping of YP 50F on activated carbon

20 g powder of AC (YP 50F, produced by Kuraray Co., Japan, originally with only 50 ppm Fe) was immersed into the solution of Fe(NO₃)₂ at 40 °C for 24 hrs. Then all the water was evaporated out at 110 °C in furnace. Thus, all Fe species remained on AC. Thereafter, the samples were further calcinated at 600 °C to decompose all nitrates in N₂ atmosphere. Controlling the amount of Fe(NO₃)₂ is

effective to control the loading of Fe on AC. Pristine AC was denoted as AC without adding Fe (although they have 50 ppm Fe), in order to distinguish ACs with intentionally doping with Fe.

2.2. Fabrication of electrode sheet and soft pack

AC or AC doped with Fe, used as electrode, were mixed uniformly with super P, adhesive (SBR and CMC) and de-ion water for 4hrs. Final slurry was pasted onto the two sides of flat Al Foil (current collector). The thickness of each side was controlled to 120 μm and dried for 24 hrs. Then electrode sheet was cut into the size of 3 cm * 5 cm and separated with cellulose membrane and sealed in an Al shell to fabricate of soft pack with 4 sheets. The gases and waters were removed by high temperature drying under vacuum. Then electrolyte of 1mol/L MeEt₃NBF₄ in PC was fed into the soft pack and staying in vacuum for 2 hrs and finally was sealed tightly.

2.3. Experimental of electrochemical charge and gas analysis

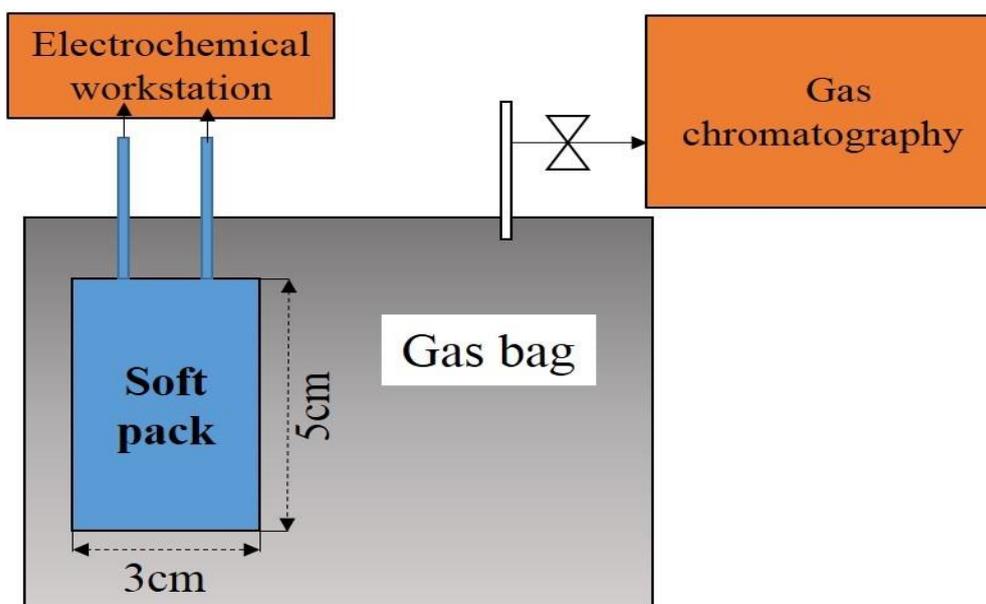


Figure 1. illustration of the in situ combined analysis of electrochemical signals and gas components.

The SC was charged at the current density of 0.1A/g at 4.0 V. Since the soft pack was inside the gas bag (Fig.1), any gases produced can be online detected by GC, equipped with the TCD and FID detector. In addition, the volume of gas bag was far larger than that of soft pack. Thus, the time-dependent volume of gases was measured to understand the stability of electrode and electrolyte in different voltages.

SC is charged at the current density of 0.1A/g at 4.0 V. Since the soft pack was inside the gas bag (Fig.1), any gases produced can be online detected by GC (GC-7890II), equipped with the TCD and FID detector. In addition, the volume of gas bag was far larger than that of soft pack, allowing the determination of the time-dependent volume of gases conveniently, but without influencing the charge

and discharge process. The time-dependent volume of gases is useful to understand the stability of electrode and electrolyte under different voltages.

2.4 Detection of electrochemical signals and the characterization of Raman and FT-IR

Cyclic voltammetry (CV curve, with an instrument of Land system) was measured from 0-4V with a current density of 0.1A/g. Specific capacitance value of electrodes was calculated based on the CV curve and the energy density of electrodes was calculated with the equation of $E=1/2CV^2$ (C: capacitance, V: voltage). Raman spectra (with an instrument of Horiba-JY, LabRAM XploRA) of electrodes were obtained under the laser of 633 nm (wave length) with the accumulation value of three-time scan. FT-IR spectra (with an instrument of Nicolet iS-5) of electrodes were obtained as scanning from the wave length of 0-4500 cm^{-1} .

3. RESULT AND DISCUSSION

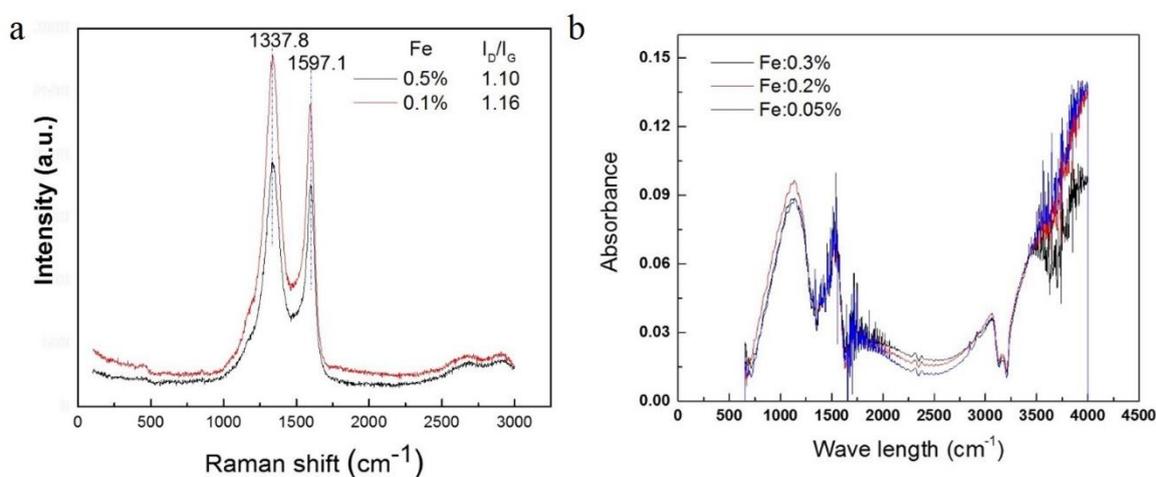


Figure 2. Raman spectra of AC doped with Fe(a), IR spectra of AC doped with Fe (b)

Raman spectra were obtained for the AC samples doping with Fe in the range of 0.1%-0.5% (Fig.2a). There is no peak shift for the D band centered at 1337.8 cm^{-1} and G band centered at 1597.1 cm^{-1} . Intensity ratios of I_D/I_G were 1.10 and 1.16 for AC with 0.1% Fe and 0.5% Fe, respectively, It suggested the doping of Fe on AC didn't result in the change of structure of Ac significantly, including the production of amorphous carbon. In addition, there are no signals of Fe species on XRD pattern, suggesting the uniform dispersion of Fe species on AC (data not shown here). From the comparison of the IR spectra (Fig.2b), the position and the intensity of peaks were very similar in the range of 500-3000 cm^{-1} for samples with or without doping with Fe. However, the intensity of peak of OH or COOH groups, in the range of 3700-4000 cm^{-1} , decreased significantly with the loading of Fe. It suggested the well dispersion and well interaction of Fe species with AC.

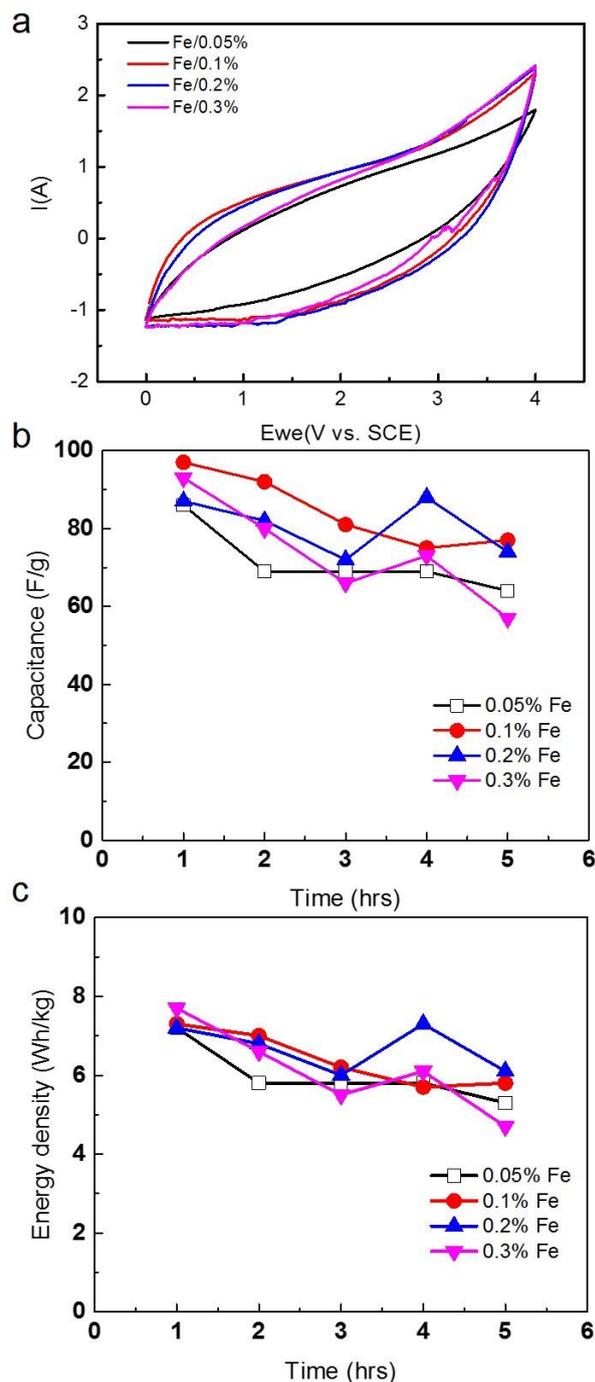


Figure 3. CV curves of Fe-doped AC in organic electrolyte at 4V (a). Time-dependent capacitance of Fe-doped AC in organic electrolyte at 4V (b). Time-dependent energy density of Fe-doped AC in organic electrolyte at 4V (c). Current density in (a), (b) and (c) is 0.1A/g

As follows, the effect of adding Fe on the capacitance response was studied and shown in Fig.3. CV curves were relatively smooth for doping 0.05%-0.3% Fe on AC (Fig.3a) when the soft pack was charged to 4V. The area enclosed under CV curves, represented the stored energy, increased with the amount of Fe on AC. Very recently, the contribution of pseudo-capacitance can be distinguished on such CV curves by varying the scanning rate and correlating the current with the capacitance [3,4],

which, however, it is not the focus in the present work. The capacitance of AC doped with Fe was in the range of 80-100 F/g in the initial stage of charge (Fig.3b). Capacitance approached to the highest value as doping 0.1% Fe on AC. These values of capacitance at 4V were nearly the same as that of pure AC operated at 2.7V. It suggested the capacitance of Fe-doped AC didn't increase drastically with the voltage, which is opposite to the trend of as using carbon nanotube (as electrode) with the increase of voltage [8]. Reasonably, AC was a material with the endohedral surface and the micropores in large amounts, which exhibited the diffusion barrier of ion inside AC, compared to that of carbon nanotube or graphene with sufficient mesopores [7,8]. With the increase of the charge and discharge time, the maximal charged voltage of SC with AC containing Fe decreased a little bit, owing to the production of gases in large amount discussed below. Similar, energy density of SC with AC doped with Fe was in the range of 7-8 Wh/kg in the initial stage of charge (Fig.1c), which is a very high value for such small soft pack of AC-based SC.

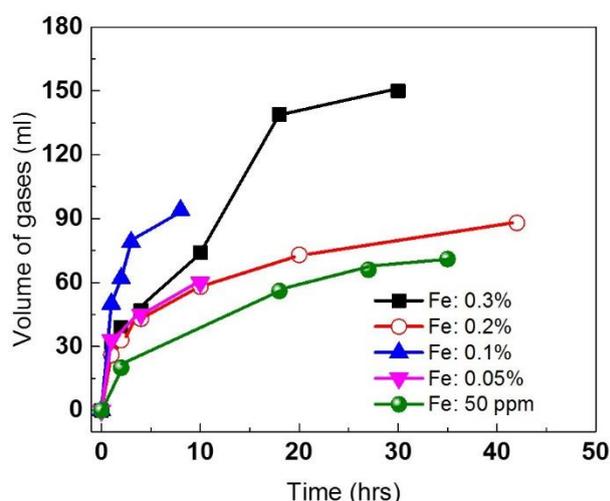


Figure 4. Time dependent volume of gases produced in different SCs with AC with different loading of Fe. The current density is 0.1A/g.

As follows, the time-dependent volume of gases was recorded and shown in Fig.4. For SC with pristine AC, the production rate of gases is 3 ml/h in the first 18 hrs. After releasing the gas and sealing SC again, the gas production rate decreased drastically in the second time charge (9 hrs in total) and in the third time charge (8 hrs in total). It suggested that the functional groups on AC, water adsorbed on AC or in electrolyte were mainly decomposed or removed in the first charge time (18 hrs in total). After that, AC-based SC work relatively stable at 4V. However, the addition of Fe on AC resulted in the drastically increase of the gas production rate up to 30 ml/h in the initial charge of 1 h (Fig.4). The total accumulated volume of gases decreased gradually with the charge time. But the gas production rate, as using AC with 0.01% Fe, is still 9 ml/h in the initial charge of 10 hrs. Similar, the average production rate with 0.02% Fe is 2.25 ml/h in the total 40 hrs. This value even approach to 3.5 ml/h in the total 35 hrs for SC with AC with 0.03% Fe. These results indicated that the addition of Fe on AC resulted in the serious decomposition of some components in SC, resulting in the release of gases in large amount.

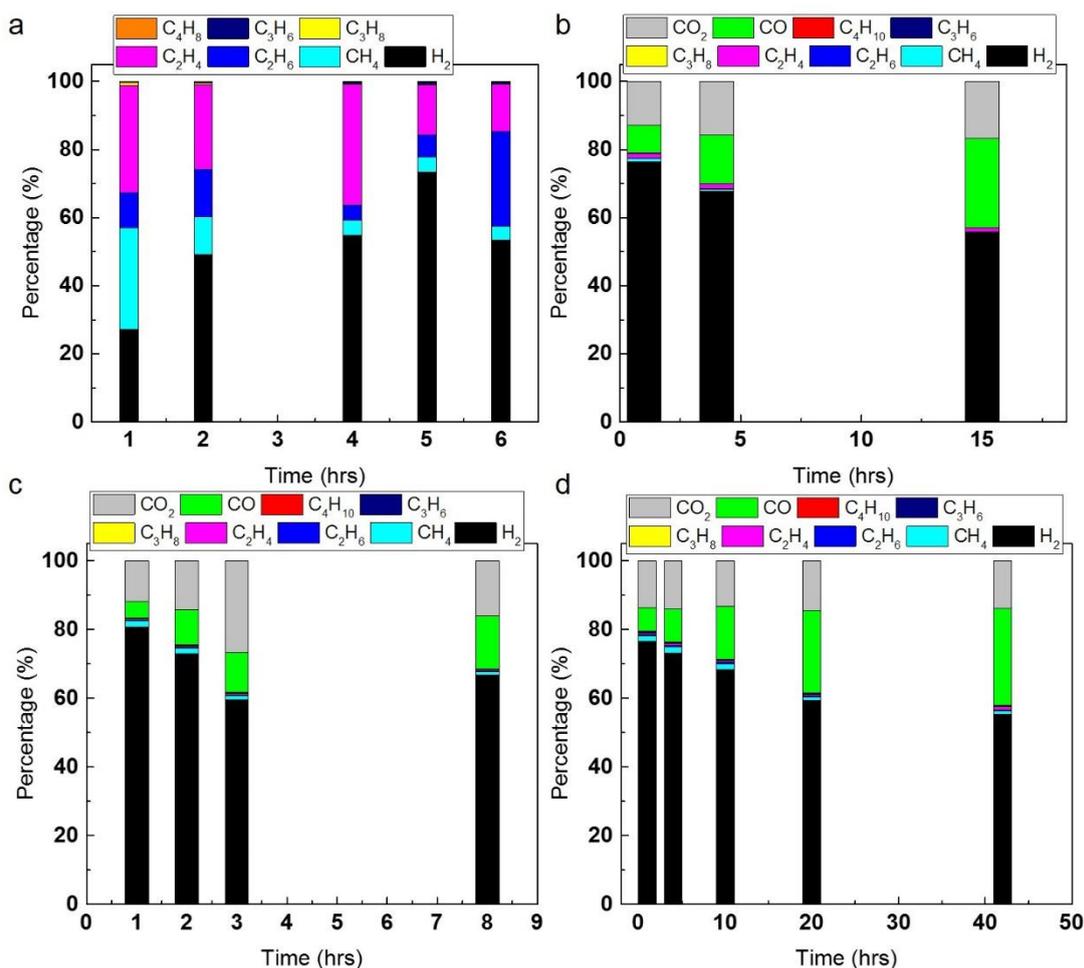


Figure 5. Time dependent of gas components with different AC. AC with only 50 ppm Fe (a); AC with 0.05% Fe (b), AC with 0.1% Fe (c) and AC with 0.2% Fe (d), respectively.

Components of gases were analyzed with the on-line GC. For SC with pristine AC, the dominant components was H_2 , CH_4 , C_2H_6 and C_2H_4 in gases, with the total volume ratio of them exceeds 97 vol.% (Fig.5a). Origin of C_2H_6 can be both from the decomposition of the salt of $MeEt_3NBF_4$ and the binder of $SBR((C_6H_5-C_5H_9)_n)$, n is the polymerization degree). But the decomposition of SBR also result in the production of aromatics in large amount, which, however, is not detectable in the present work. In this case, these hydrocarbons with low carbon number should originated mostly from the decomposition of the sale of $MeEt_3NBF_4$. Except that, other organic components ($PC(CH_3-C_3H_5O_3)$, and $CMC([C_6H_7O_2(OH)_x(OCH_2COONa)_y]_n)$, $x+y=1$, n is the polymerization degree)) were unable to provide methyl-, ethyl- groups in such a large amount. However, with the increase of charge and discharge time, the percentage of H_2 increased constantly, while the percentage of CH_4 decreased sustainably. In addition, the percentage of H_2 decreased accordingly with the increase of the total percentage of paraffins. These results suggested that H_2 is consumed when the formation of CH_4 or C_2H_6 is enhanced. In previous work, CO and propene was the dominant product of gases in SC with AC as electrode and organic electrolyte using PC as solvent [11-14]. Origin of propene was directly attributed to the decomposition of PC. In sharp contrast, C_3H_6 and C_3H_8 was not the dominant product in gases with PC-based electrolyte in the present work. It

suggested that, salt of $\text{MeEt}_3\text{NBF}_4$ was much easily decomposed, compared to PC, with the present AC sample. However, the gas components were significantly different as adding Fe on AC (Fig.5b-5d). The addition of 0.05-0.3% Fe resulted in the change of the dominant gases from hydrocarbons and H_2 to be H_2 , CO and CO_2 . The percentage of the three gases (H_2 , CO and CO_2) exceeds 97% in all cases. Percentage of hydrocarbons, however, was in a negligible amount. These results suggested that salt of $\text{MeEt}_3\text{NBF}_4$ and PC were not decomposed any more, in presence of Fe species on AC.

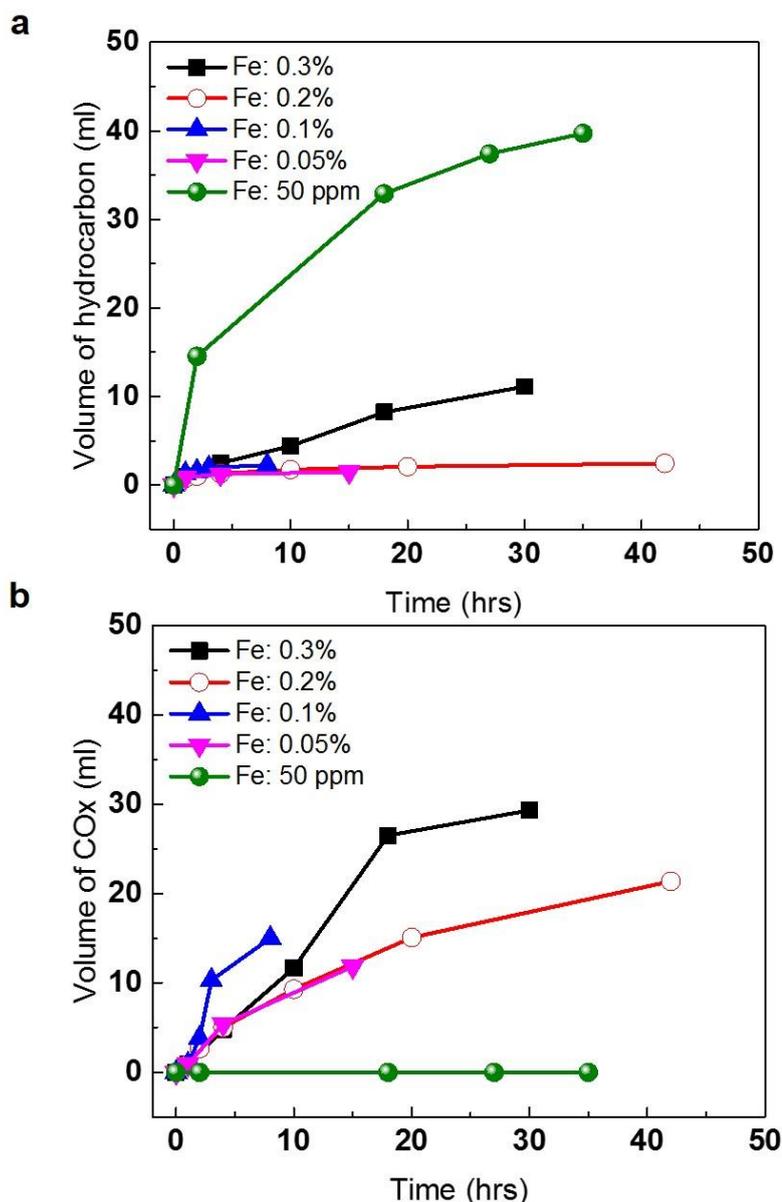


Figure 6. Time dependent volume of hydrocarbons (accumulated value) with different AC (a), Time dependent volume of COx (accumulated value) with different AC (b).

The volume of hydrocarbons or COx ($\text{CO} + \text{CO}_2$) were calculated and shown in Fig.6. It is clear that the amounts of hydrocarbons produced from the decomposition of salt and PC were very high. The accumulated volume of hydrocarbons as using pristine AC (with only 50 ppm Fe) is 15 ml, 32 ml, 40 ml at 1 h, 18 hrs and 35 hrs, respectively (Fig.6a). In sharp contrast, the accumulated volume of

hydrocarbons was negligible as using AC doped with 0.05% -0.2% Fe. In addition, the volume of hydrocarbons is still lower than 10 ml at 30 hrs, even increasing the dope amount of Fe to 0.3%. Similar, the accumulated volume of COx was in the range of 30 ml at 30 hrs for using AC doped with 0.3% Fe (Fig.6b). In contrast, no CO and CO₂ were produced if using pristine AC. These data suggested a new decomposition phenomenon of components of SC as operated in high voltage. The effect of Fe become more and more significant with the doping amount of them. Its effect is much similar to the catalytic decomposition effect in many heterogeneous catalytic processes, as remaining a monodispersed state on AC. Addition of 0.3% Fe on AC resulted in the production of COx and hydrocarbons in larger amounts, compared to those from AC doped with 0.05%-0.2 % Fe. It is noticed that the self-decomposition of salt was previously reported under high voltage [19]. However, the previous work didn't report the fact that the salt remained stable, but CMC was seriously decomposed in the presence of Fe.

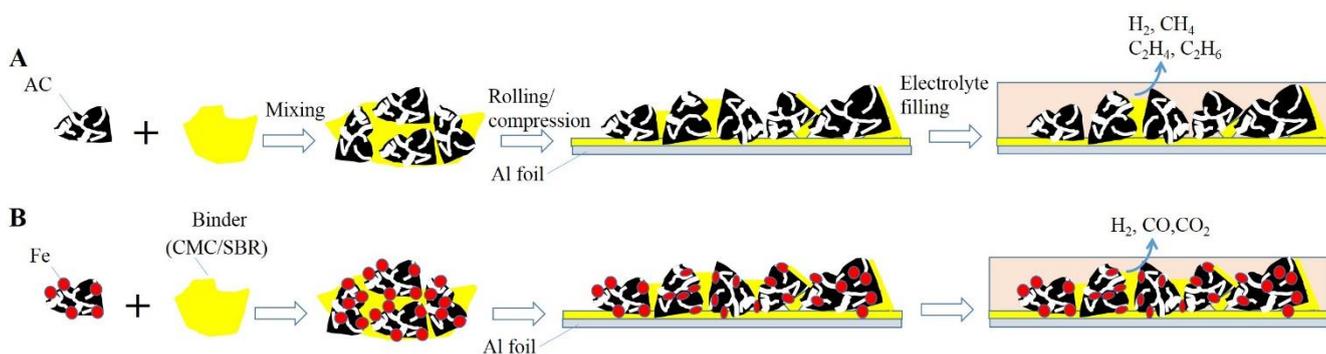


Figure 7. A mode of Fe on catalyzing binders or organic electrolytes, depending on their position and hydrophilicity.

Here we proposed, for the first time, the different contact effects of Fe with CMC, salt of electrolyte may influence the decomposition process. As show in Fig.7, binder of SBR and CMC, soluble in water, was firstly mixed with AC to be a uniform slurry. Then the slurry was pasted onto the Al foil by rolling and compression. After drying, AC particles contacted tightly with Al foil via the binder layer. In addition, binder existed around various AC particles to form a compact sheet of electrode. Some binder were able to penetrate into the large pores of AC, via the effect of capillary filling. Therefore, there have large probabilities of binders contacting with Fe on AC particles. Actually, the component of binder (CMC and SBR), in a well-mixed state, had similar opportunities interacting with Fe species. But SBR and CMC exhibited the hydrophobic property and hydrophilic property, respectively. In comparison, CMC was easily accessible to Fe species on AC. In addition, SBR had a higher chemical stability than CMC. In this case, the possibility of the decomposition of CMC by Fe species, was larger than on the SBR. More important, the electrode, which integrated with Al foil sheet and membrane together, is firstly set, then the electrolyte is finally filled into the SC in the common processing steps of SC. Thus, the position inside AC, firstly occupied by binders, was difficult to be replaced by the electrolyte consisting of PC, which is a hydrophobic solvent. In this

case, when SC was charged, the voltage exposed provides the energy for Fe to catalyze anything around them. Naturally, CMC were firstly catalyzed by Fe species, rather than the salt or PC.

On the other hand, if absence of Fe, salt and solvent of electrolyte was firstly decomposed by of AC with oxygen-containing functional groups [11-14]. Such weak catalytic effect, compared to the Fe effect, explained well that less amount of gases was produced if absence of Fe. Our mode, for the first time, stressed the effect of the contact position and hydrophilicity/ hydrophobicity of different components inside SC, which were not fully considered previously. Apparently, such “buckets effect” depends on the doping amount of Fe (Fig.6a). Such analysis is also useful to the system of using new carbon nanomaterials (carbon nanotube or graphene) [8, 20], considering the effect of metal impurities would exhibited similar effect on binders or electrolyte [21, 22]. Further investigation is needed to understand the addition effect of Fe on the stability of other types of salt and binders.

4. CONCLUSIONS

As doping of 0.05%-0.3% of Fe on AC, sufficient information of gas from the decomposition of specific components with the associated electrochemical signals were obtained as charging and discharging at 4V. H₂ and hydrocarbons were the dominant gas product as using AC without Fe, owing to the decomposition of salt of organic electrolyte. However, the dominant gases changed to be H₂, CO and CO₂ as using AC doped with 0.05%-0.3% Fe. The decomposition of CMC in presence of Fe contributed to the increased capacitance and energy density, but such effect is unstable. As carefully analyzing the processing steps and the hydrophilic or hydrophobic properties of the binders and electrolyte, A mode considering the different contact effects of components with Fe species and different stability of them was established in high voltage. The combined analysis of gases and capacitance signals, under an accelerated aging condition, provides deep insight on the “buckets effect” in SC system involving into electrode, electrolyte, metal impurities and binders.

References

1. M. Inagaki, H. Konno and O. Tanaike, *J Power Sources*, 195(2010)7880.
2. A.S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon and W.V.Schalkwijk, *Nat. Mater.*, 4(2005)366.
3. Y. Xia, T. S. Mathis, M.Q. Zhao, B. Anasori, A. Dang, Z.H.Zhou, H.S. Cho, Y. Gogotsi and S. Yang. *Nature*, 557(2008)409.
4. H.T. Sun, L. Mei, J.F. Liang, Z.P. Zhao, C. Lee, H.L. Fei, M.N. Ding, J. Lau, M.F. Li, C. Wang, X. Xu, G.L. Hao, B. Papandrea, I. Shakir, B. Dunn, Y. Huang and X.F. Duan, *Science*, 356 (2017) 599.
5. C. Zheng, W.Z. Qian, C.J. Cui, Q. Zhang, Y.G. Jin, M.Q. Zhao, P.H. Tan and F. Wei, *Carbon*, 50(2012) 5167.
6. X. W. Yang, C. Cheng, Y. F. Wang, L. Qiu and D. Li, *Science*, 341(2013) 534.
7. C.J. Cui, W.Z. Qian, Y.T. Yu, C.Y. Kong, B. Yu, L. Xian and F. Wei, *J. Am. Chem. Soc.*, 136(2014) 2256.
8. A. Izadi-Najafabadi, S. Yasuda, K. Kobashi, T. Yamada, D.N. Futaba, H. Hatori, M. Yumura, S. Iijima and K. Hata, *Adv. Mater.*, 22(2010) E235.
9. Z.H. Zhao, S.M. Hao, P. Hao, Y.H. Sang, A. Manivannan, N.Q. Wu and H. Liu, *J. Mater. Chem. A*, 3(2015) 15049.

10. J. Li, N. Wang, J. Deng, W.Z. Qian and W. Chu, *J. Mater. Chem. A*, 6(2018) 13012.
11. M. Hahn, A. Wursig, R. Gallay, P. Nova'k and R. Ko'tz, *Electrochem. Commun.*, 7(2005) 925.
12. R. Ko'tz, M. Hahn, P. Ruch and R. Gallay, *Electrochem. Commun.*, 10(2008) 359.
13. P. Kurzweil and M. Chwistek, *J Power Sources*, 176(2008)555.
14. P. Aza'is, L. Duclaux, P. Florian, D. Massiot, M.A.Lillo-Rodenas , A. Linares-Solano, J.P. Peres, C. Jehoulet and F. B'egu'in, *J Power Sources*, 171(2007)1046.
15. K. Gadkaree and J. Liu, *USA patent*, 2015, US9006136B2.
16. Y.T. Ju, M.Y. Cho, M.H. Kim, J.W. Lee, S.Y. Park, B.H. Choi and K.C. Roh, *J. Ceramic Processing Research*, 13(2012)s159.
17. J. Li, Z. Xu and Z.A. Zhang, *RSC Adv.*, 28(2018)32188.
18. W. Lv, Z. J. Li, Y.Q. Deng, Q.H. Yang and Kang, F.Y. *Energy Storage Mater.*, 2 (2106)107.
19. T. Yoon, M.S. Milien, B.S. Parimalam and B.L. Lucht, *Chem. Mater.* 29(2017)3237.
20. C. Zheng, W.Z.Qian, Y.T. Yu, and F. Wei, *Particuology*, 11(2013)409.
21. W. Huang, Y. Wang, G.H. Luo and F. Wei, *Carbon*, 41 (2003) 2585.
22. Y. Q. Xu, H.Q. Peng, R. H. Haug and R.E. Smalley, *Nano Lett.*, 5 (2005) 163.

© 2019 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).