Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

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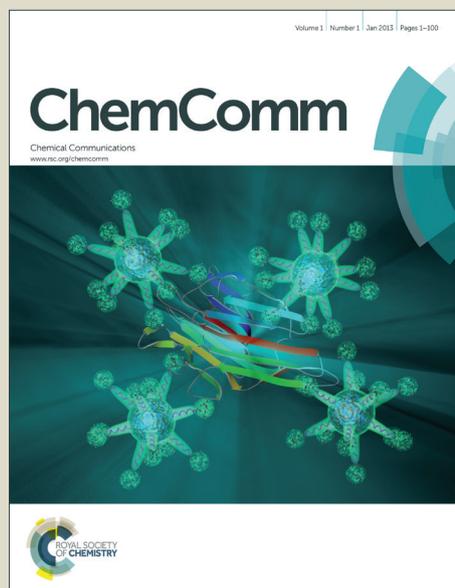
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Fullerenes: Non-transition Metal Cluster For Rechargeable Magnesium Battery Cathode [†]

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We discovered that non-transition metal clusters have great potential as rechargeable Mg battery cathodes. Fullerene (C_{60}), one of the prototype materials, was discharged and recharged with remarkable rate capability. This unique rate performance is attributed to its capability to delocalize electrons on the entire cluster rather than to individual atom.

Recently, batteries utilizing the shuttle of multivalent light weight ions, such as Mg, Ca and Al, have gained increasing interest due to their potentials to go beyond current Li-ion battery technology.[1-4] Among them, the rechargeable Mg battery has received much attention owing to the earth abundance of element Mg as well as the high volumetric capacity of metallic Mg anode.[1,2,4-8] However, searching for a cathode has become the major hurdle in the development of practical Mg battery. Compared to monovalent Li^+ ions, the mobility of divalent Mg^{2+} ions can be significantly lower in intercalation-type cathodes.[9] The sluggish diffusion leads to much slower Mg insertion/removal kinetics, or even prevents a practical insertion/removal.[10,11] Various approaches have been proposed to overcome the diffusion problem, including decreasing the particle size of active materials[12], shielding Mg^{2+} from electrostatic interaction[13] and exploring materials with specific crystal structures.[14] But to date, Chevrel phase (CP, Mo_6S_8) is the only reported intercalation-type cathode with high cyclability and rate capability.[15] The good rate performance of CP was attributed to the unique Mo_6 clusters in its structure, for which the redistribution of the bivalent cation charge changes the formal charge of individual Mo cation only by $2/3e$.[16,17] As a consequence of this charge distribution mechanism, CP easily compensates the charge imbalance from the introduction of bivalent ions, and achieves faster Mg^{2+} intercalation kinetics.[15]

Most classical intercalation-type cathodes rely on transition metal (TM) compounds, in which the electrochemical charge (discharge) is accomplished by the oxidation (reduction) of TM ions.[18] However, the valence variation of TM ions is typically associated with the necessary change of local bonding environment,[19] which may strongly limit the mobility of divalent Mg^{2+} ions. In order to overcome this limitation, here we investigate a novel concept for Mg battery cathode, which completely avoids the usage of TM species. The new cathode material contains a group of non-transition metal atoms bonding together by inter-atomic forces to form cluster. The best-known example of such materials is the fullerene, C_{60},

which forms entirely by the covalently bonded carbon atoms.[20] In this Communication, we report the electrochemical activity of prototype C_{60} cathode in a rechargeable Mg battery. Remarkably, C_{60} cathode shows beautiful plateaus and good rate performance, which is attributed to its unique capability to delocalizing electrons on the entire cluster rather than to individual atoms.
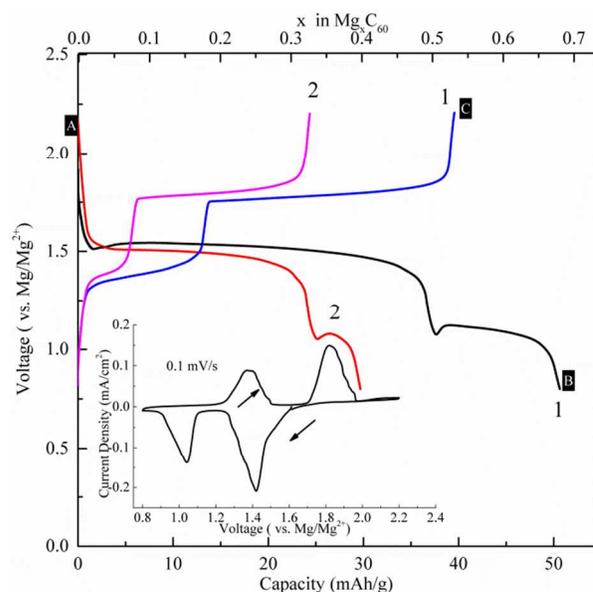

Figure 1 Galvanostatic curves for the C_{60} cathode at the current density of 19 uA/cm². The inset shows the corresponding cyclic voltammogram (CV) curve. A, B and C indicate the electrochemical states of pristine, discharged and recharged electrodes, respectively.

The fullerene electrode was prepared using commercial available C_{60} powder as described in the method part in ESI. The electrochemical activity of C_{60} cathode in the Mg battery cell was evidenced in the galvanostatic cycling test. In the discharge, the voltage quickly reached a flat plateau at 1.4 V. After the capacity reached 37 mAh/g (~0.5 Mg per C_{60}), the voltage dropped to the second plateau at 1.1 V and reached another capacity of 13 mAh/g before cutting off at 0.8 V. The whole discharge capacity was 50 mAh/g (~0.68 Mg per C_{60}). The recharge process also presented two voltage plateaus at 1.3 and 1.8 V, respectively. The charge capacity was 41 mAh/g, slightly less than the discharge capacity. This might be due to the trapping of Mg ions at certain sites after discharge, which does not participate in the charge. The reversibility of the C_{60}

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cathode was further confirmed by the cyclic voltammetry (CV) scan. Two redox couples were observed at 1.4/1.8 V and 1.1/1.4 V, which can be assigned to the redox couple of C_{60}/C_{60}^- and C_{60}^-/C_{60}^{2-}.

Many reported Mg battery suffered with large discharge-charge voltage hysteresis. For instance, the voltage hysteresis for α-MnO_2 cathode was ~1.0 V, while for WSe_2 cathode it was around 0.7 V.[7, 21] Interestingly, the discharge-charge voltage hysteresis for C_{60} cathode was only ~0.2-0.4 V. This is quite comparable to the CP cathode, which showed a hysteresis of ~0.2 V. It is generally accepted that the discharge-charge voltage hysteresis originates from complex kinetic limitations.[22] The low voltage hysteresis of the C_{60} electrode implies high kinetics for the migration of Mg ions, which has been proved with a solid state measurement recently.[23]
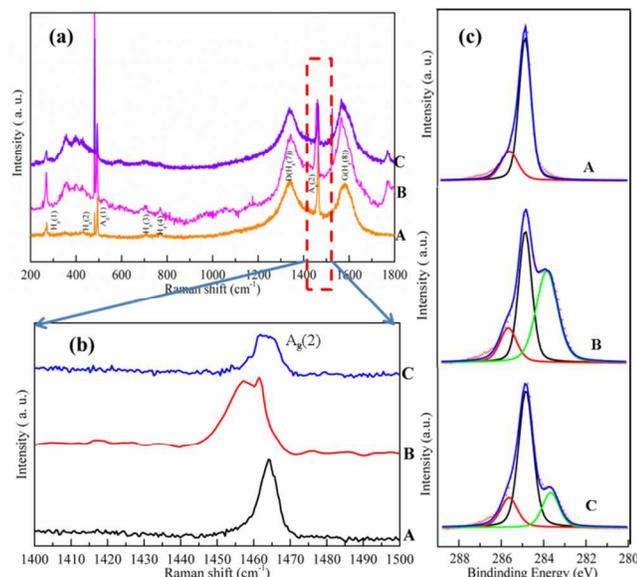

Figure 2 (a) Raman spectra of the C_{60} electrodes at different electrochemical states. The modes are labelled. The $H_g(7)$ and $H_g(8)$ modes are overlapped with D band and G band of carbon black in the electrode, respectively. (b) Zoom in spectra for $A_g(2)$ peaks. (c) C1s XPS spectra of C_{60} electrodes. The three peaks at 285.6 (red), 284.7 (black) and 283.7 eV (green) correspond to carbonate, carbon and magnesiated carbon, respectively.

To reveal the magnesiation mechanism of the C_{60} cathode, we employed Raman spectroscopy analysis, which has been a key experimental technique for the C_{60} study due to its strong Raman response. In the electrochemical discharge and charge of C_{60}, the charge transfer can be characterized by the shift of Raman peaks. Particularly, $A_g(2)$ pinch mode is a good probe for this purpose, whose position scales with the amount of charges on the C_{60} cluster.[24, 25] One elementary charge transfer on the C_{60} molecule yields a down-shift of $A_g(2)$ peak by *ca.* 6 cm^{-1}.[24] As shown in Figure 2a, the $A_g(2)$ mode showed an average downshift of 8 cm^{-1} after discharge, corresponding to the transfer of ~1.33e to C_{60} cluster. This value matches excellently with the discharge capacity (~0.68Mg or ~1.36e). After recharge the $A_g(2)$ peak up-shifted, indicating the loss of electrons from C_{60} molecule. The charge transfer to C_{60} cluster was further confirmed by X-ray photoelectron spectroscopy (XPS) measurements (Figure 2b). The pristine electrode showed one main response at 284.7 eV, which is attributed to 1s excitation of elementary carbon (note C 1s signals from C_{60} and carbon black are overlapped). For the discharged electrode, a new response centered at 283.7 eV appeared, which is assigned to negative charged carbon.[26] After recharge, the intensity of shoulder peak at 283.7 eV decreased, suggesting Mg ion partially extracted from the C_{60} cathode.
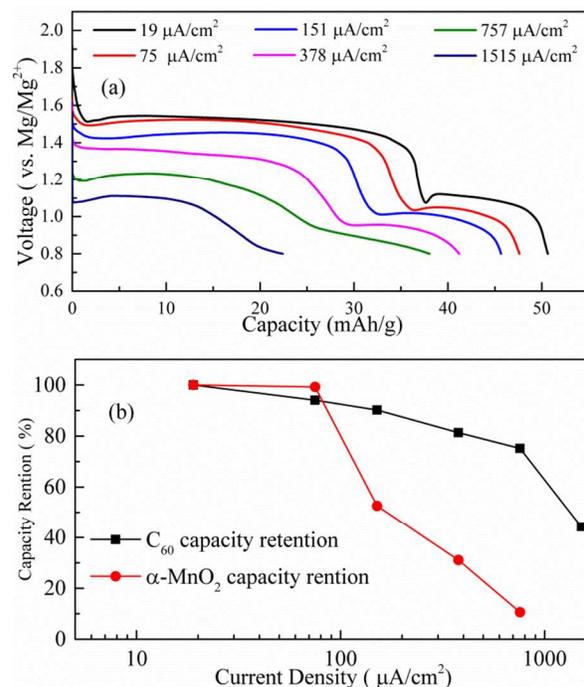

Figure 3 (a) Galvanostatic discharge curves for the C_{60} cathode at different current density rates. (b) Capacity retention of C_{60} and α-MnO_2 electrodes at different current density. The capacities for C_{60} and α-MnO_2 operated at 19 uA/cm^2 were normalized to 100%, respectively.

Combining the evidences from Raman and XPS measurements, it is clear that the C_{60} cluster accepts electrons and balances the charge neutrality when guest Mg^{2+} ions are shuttled to the cathode in the discharge and vice versa in the charge. C_{60} has threefold degenerated lowest unoccupied molecular orbital, which easily obtains electrons in the delocalized pseudo-π orbital.[27] Therefore, the delocalized extra electron changes the formal valence of individual carbon by 1/60e rather than being localized on any individual carbon atom. Levi et al. speculated that the delocalization of extra electrons brought by the magnesiation on a group of ions is crucial to improve Mg^{2+} mobility in cathode materials.[16,17] Indeed, the C_{60} cathode showed a remarkable rate capability compared to other Mg battery cathodes. Figure 3 (a) shows the discharge profiles recorded at different current densities. Even at the current density of 1515 uA/cm^2, the C_{60} cathode still retained 44% of its capacity operated at 19 uA/cm^2. For comparison, we also tested the rate performance of a transition metal based cathode, α-MnO_2 (Figure S1). At a current density of 151 uA/cm^2 the capacity of α-MnO_2 only attained 50% of its capacity operated at 19 uA/cm^2. The capacity further dropped down to less than 10 % when the current density increased to 757 uA/cm^2 (Figure 3b). Apparently the rate performance of C_{60} cathode is considerably better than that of α-MnO_2 cathode. The excellent electrochemical performance of C_{60} should be related to their cluster structure.

The rate-dependent cyclability of C_{60} cathode is shown in Figure 4. Interestingly, the cyclabilities at high current densities seem to be better than those at low current densities. One of the main possible reason is that unlike conventional electrode material, such as silicon, C_{60} is known to dissolve in organic solvents; especially the formation of $M^{+n}C_{60}^{-n}$ (M=Mg in this study) can cause serious dissolution of the electrode.[28,29] At lower rates a longer charge time may result in greater loss of C_{60}, consequently leading to poor cyclability. Another reason caused the capacity fading might be that, as revealed by XRD and TEM analysis, the C_{60} electrode showed

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certain degree of amophorization after cycling (Figure S2). This type of the structure and morphology change may also contribute to the capacity drop. Although the detailed mechanism about the cyclability is still under investigation, we note that the current study employed commercial C_{60} without any optimization. It is reasonable to anticipate that there is plenty of room for the improvement of cyclability. For instance, adding protection layer on the cathode can minimize the dissolution of the active material.[30,31] Another strategy for the optimization is to modify C_{60} with functional groups, which can also effectively tune its physical and chemical properties.[32]
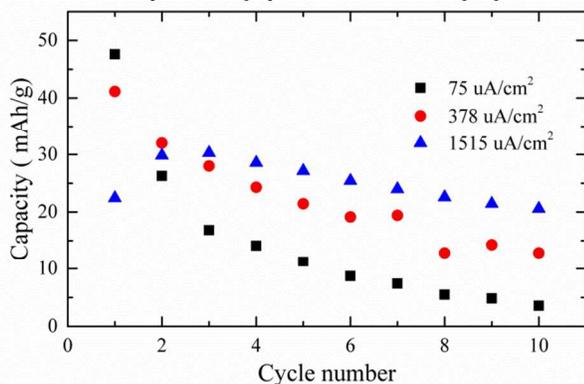

Figure 4 Galvanostatic cycling performances for the C_{60} cathode at different current densities .

Finally, the performances of other carbon based materials in Mg battery were also tested, including graphite, carbon nanotubes and carbon black. We failed to observe any voltage plateau with apparent capacity (< 5 mAh/g). In contrast, another cluster-type material, C_{70}, clearly showed flat voltage profile as well as characteristically low discharge-charge voltage hysteresis (Figure S3). This comparison further confirms that the electrochemical performance of C_{60} and C_{70} is related to their unique cluster structure that enables the delocalization of extra electrons. It strongly suggests that we may extend our concept to use other materials containing non-transition metal clusters as rechargeable Mg battery cathodes.

As shown in this study, a key concern of C_{60} as cathode material for rechargeable Mg battery is its relatively low capacity. Previous studies suggest theoretically one C_{60} molecular can accept up to 6 electrons and consequently combine 3 Mg^{2+} ions.[33] However, the electrochemical reaction between C_{60} and Mg^{2+} is a stepwise reaction, which indicates some steps will appear at very low potential vs. Mg/Mg^{2+}, or even can't be electrochemically reached because they might be lower than the Mg deposition potential (-2.31 V vs. SHE). As a cathode material, only the capacity at high voltage is useful and the capacities at low potential have to be scarified. In order to increase the working of potential of C_{60} based cathode, one possible countermeasure is to add certain function groups in terms of changing hybridization of the carbon. For example, the first reduction potentials of C_{60} and $C_{60}F_{18}$ are (in dichloromechanes, vs. SCE) -0.59 and 0.04 V, respectively.[34] We also noticed that only the capacity of first plateau reached the theoretical value, 37 mAh/g ($\sim$ 1 e transfer), but all other plateaus related capacity were not. Similar phenomenon has also been observed in Chevrel phases. It might be related Mg ions bonding to different sites at C_{60} cages and some Mg ions are trapped. The detailed mechanism is under investigation.[35]

In this communication we proposed a concept to use materials containing non-transition metal cluster as rechargeable Mg battery. As a proof-of-concept the prototype C_{60} cathode showed a capacity of ~50 mAh/g when discharge to 0.8 V. The Raman and XPS measurements suggested the extra electrons brought by the magnesiation are delocalized on the entire C_{60} cluster which leads to remarkable rate performance of C_{60} cathode. Considering the large family of atomic clusters made of non-transition metal elements, our current work opens a new horizon for the development of Mg battery cathode. In addition, this concept may also provide a solution for other multivalent batteries such as Ca or Al, thereby shedding light on the next generation of battery technology.

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