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Understanding the Electrochemical Mechanism of K- α MnO₂ for Magnesium Battery Cathodes

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Fullerenes: non-transition metal clusters as rechargeable magnesium battery cathodes†

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We discovered that non-transition metal clusters have great potential as rechargeable Mg battery cathodes. Fullerene (C₆₀), one of the prototype materials, was discharged and recharged with a remarkable rate capability. This unique rate performance is attributed to its capability to delocalize electrons on the entire cluster rather than to individual atoms.

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 the element Mg as well as the high volumetric capacity of the metallic Mg anode.^{1,2,4–8} However, the search for a cathode has become the major hurdle in the development of practical Mg batteries. Compared to monovalent Li⁺ ions, the mobility of divalent Mg²⁺ 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 Mg²⁺ from electrostatic interaction¹³ and exploring materials with specific crystal structures.¹⁴ But to date, the Chevrel phase (CP, Mo₆S₈) is the only reported intercalation-type cathode with high cyclability and rate capability.¹⁵ The good rate performance of the CP was attributed to the unique Mo₆ clusters in its structure, for which the redistribution of the bivalent cation charge changes the formal charge of the individual Mo cation only by 2/3e.^{16,17} As a consequence of this charge distribution mechanism, the CP easily compensates the charge imbalance by the introduction of bivalent ions, and achieves faster Mg²⁺ 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 in the local bonding environment,¹⁹ which may strongly limit the mobility of divalent Mg²⁺ ions. In order to overcome this limitation, here we investigate a novel concept for Mg battery cathodes, 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 clusters. The best-known example of such materials is fullerene, C₆₀, which forms entirely by the covalently bonded carbon atoms.²⁰ In this Communication, we report the electrochemical activity of a prototype C₆₀ cathode in a rechargeable Mg battery. Remarkably, the C₆₀ cathode shows beautiful plateaus and good rate performance, which are attributed to its unique capability of delocalizing electrons on the entire cluster rather than of individual atoms.

The fullerene electrode was prepared using commercially available C₆₀ powder as described in the method section in the ESI.† The electrochemical activity of the C₆₀ 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 mA h g^{−1} (~0.5 Mg per C₆₀), the voltage dropped to the second plateau at 1.1 V and reached another capacity of 13 mA h g^{−1} before cutting off at 0.8 V. The whole discharge capacity was 50 mA h g^{−1} (~0.68 Mg per C₆₀). The recharge process also presented two voltage plateaus at 1.3 and 1.8 V, respectively. The charge capacity was 41 mA h g^{−1}, 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 C₆₀ 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 C₆₀/C₆₀[−] and C₆₀[−]/C₆₀^{2−} (Fig. 1).

Many reported Mg batteries suffered large discharge–charge voltage hysteresis. For instance, the voltage hysteresis for an α-MnO₂ cathode was ~1.0 V, while for the WSe₂ cathode it was around 0.7 V.^{7,21} Interestingly, the discharge–charge voltage hysteresis for the C₆₀ cathode was only ~0.2–0.4 V. This is quite

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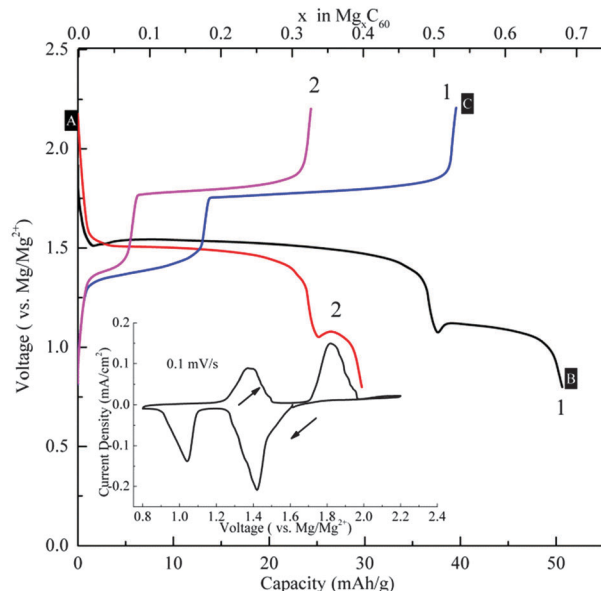


Fig. 1 Galvanostatic curves of the C_{60} cathode at the current density of $19 \mu A cm^{-2}$. The inset shows the corresponding cyclic voltammogram (CV) curve. A, B and C indicate the electrochemical states of pristine, discharged and recharged electrodes, respectively.

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 by a solid state measurement recently.²³

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 the $A_g(2)$ peak by *ca.* $6 cm^{-1}$.²⁴ As shown in Fig. 2a, the $A_g(2)$ mode showed an average downshift of $8 cm^{-1}$ after discharge, corresponding to the transfer of $\sim 1.33e$ to the C_{60} cluster. This value matches excellently with the discharge capacity (~ 0.68 Mg or $\sim 1.36e$). After recharge the $A_g(2)$ peak up-shifted, indicating the loss of electrons from the C_{60} molecule. The charge transfer to the C_{60} cluster was further confirmed by X-ray photoelectron spectroscopy (XPS) measurements (Fig. 2b). The pristine electrode showed one main response at 284.7 eV, which is attributed to 1s excitation of elementary carbon (note that 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 negatively charged carbon.²⁶ After recharge, the intensity of the shoulder peak at 283.7 eV decreased, suggesting the partial extraction of Mg ions from the C_{60} cathode.

Combining the evidence 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

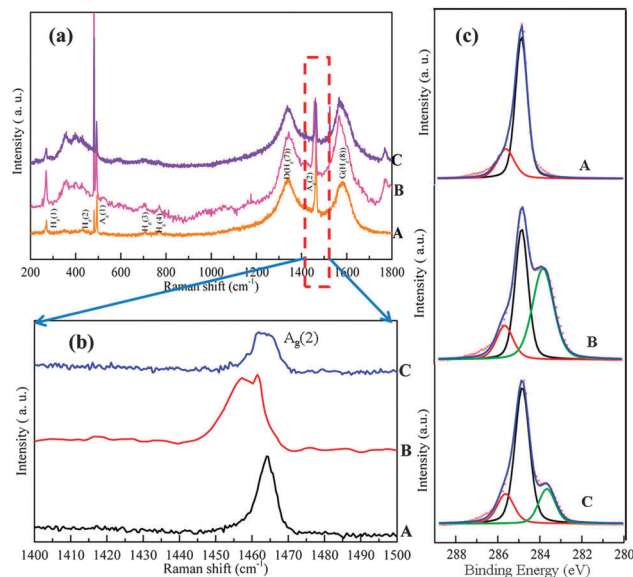


Fig. 2 (a) Raman spectra of the C_{60} electrodes at different electrochemical states. The modes are labelled. The $H_g(7)$ and $H_g(8)$ modes are overlapped with the D band and the G band of carbon black in the electrode, respectively. (b) Zoom in spectra of $A_g(2)$ peaks. (c) C1s XPS spectra of C_{60}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

shuttled to the cathode in the discharge and *vice versa* in the charge. C_{60} has a 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. Fig. 3a shows the discharge profiles recorded at different current densities. Even at the current density of $1515 \mu A cm^{-2}$, the C_{60} cathode still retained 44% of its capacity operated at $19 \mu A cm^{-2}$. For comparison, we also tested the rate performance of a transition metal based cathode, $\alpha-MnO_2$ (Fig. S1, ESI†). At a current density of $151 \mu A cm^{-2}$ the capacity of $\alpha-MnO_2$ only attained 50% of its capacity operated at $19 \mu A cm^{-2}$. The capacity further dropped down to less than 10% when the current density increased to $757 \mu A cm^{-2}$ (Fig. 3b). Apparently the rate performance of the C_{60} cathode is considerably better than that of the $\alpha-MnO_2$ cathode. The excellent electrochemical performance of C_{60} should be related to its cluster structure.

The rate-dependent cyclability of the C_{60} cathode is shown in Fig. 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 materials, 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

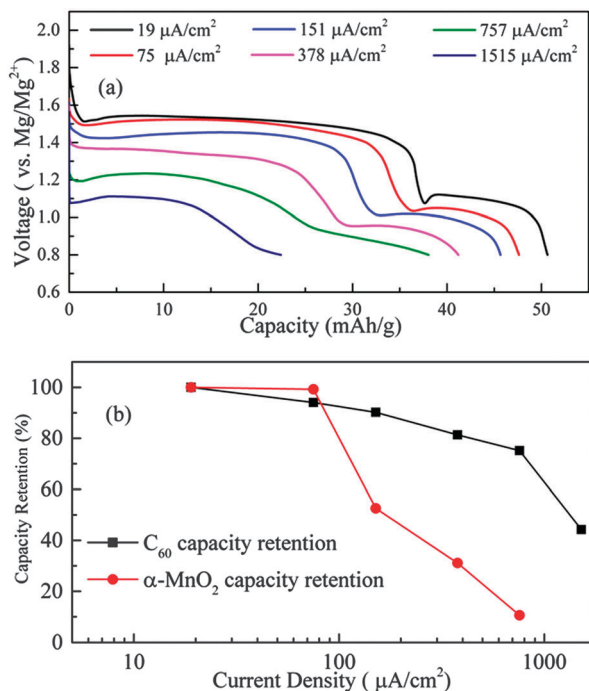


Fig. 3 (a) Galvanostatic discharge curves of the C₆₀ cathode at different current density rates. (b) Capacity retention of C₆₀ and α-MnO₂ electrodes at different current densities. The capacities of C₆₀ and α-MnO₂ operated at 19 μA cm⁻² were normalized to 100%, respectively.

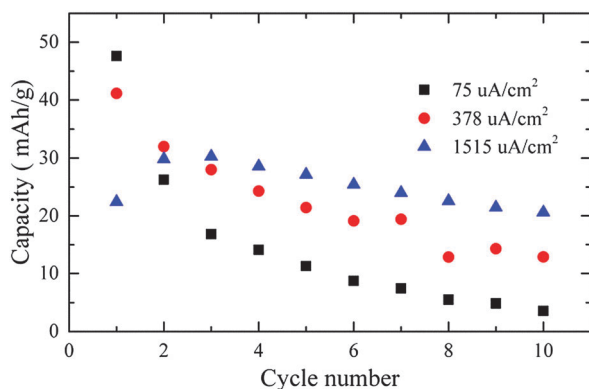


Fig. 4 Galvanostatic cycling performances of the C₆₀ cathode at different current densities.

leading to poor cyclability. Another reason caused the capacity fading might be that, as revealed by XRD and TEM analysis, the C₆₀ electrode showed a certain degree of amorphization after cycling (Fig. S2, ESI†). This type of the structural 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 C₆₀ without any optimization. It is reasonable to anticipate that there is plenty of room for the improvement of cyclability. For instance, adding a protection layer on the cathode can minimize the dissolution of the active material.^{30,31} Another strategy for the optimization is to modify C₆₀ with functional groups, which can also effectively tune its physical and chemical properties.³²

Finally, the performances of other carbon based materials in Mg batteries were also tested, including graphite, carbon nanotubes and carbon black. We failed to observe any voltage plateau with apparent capacity (<5 mA h g⁻¹). In contrast, another cluster-type material, C₇₀, clearly showed a flat voltage profile as well as characteristically low discharge-charge voltage hysteresis (Fig. S3, ESI†). This comparison further confirms that the electrochemical performance of C₆₀ and C₇₀ 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 C₆₀ as a cathode material for rechargeable Mg batteries is its relatively low capacity. Previous studies suggest that theoretically one C₆₀ molecule can accept up to 6 electrons and consequently combine 3 Mg²⁺ ions.³³ However, the electrochemical reaction between C₆₀ and Mg²⁺ is a stepwise reaction, which indicates some steps will appear at very low potential vs. Mg/Mg²⁺, 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 sacrificed. In order to increase the working potential of the C₆₀ based cathode, one possible countermeasure is to add certain functional groups in terms of changing the hybridization of the carbon. For example, the first reduction potentials of C₆₀ and C₆₀F₁₈ are (in dichloromethanes, vs. SCE) -0.59 and 0.04 V, respectively.³⁴ We also noticed that only the capacity of the first plateau reached the theoretical value, 37 mA h g⁻¹ (~1e transfer), but all other plateaus related capacity were not. A similar phenomenon has also been observed in Chevrel phases. It might be related to Mg ions bonding to different sites at C₆₀ 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 clusters as rechargeable Mg batteries. As a proof-of-concept the prototype C₆₀ cathode showed a capacity of ~50 mA h g⁻¹ when discharged to 0.8 V. The Raman and XPS measurements suggested the extra electrons brought by the magnesiation are delocalized on the entire C₆₀ cluster, which leads to a remarkable rate performance of the C₆₀ 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 cathodes. 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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